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# ***JPRS Report***

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THERMAL RESISTANCE COMPOSITE MATERIALS SEMINAR

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THERMAL RESISTANCE COMPOSITE MATERIALS SEMINAR

906C7532 Tokyo KYOKUGEN KANKYO YO TAINETSU FUKUGO ZAIRYO in  
Japanese 20 Jan 90 pp 1-97

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Thermal Resistance Composite Materials in Hazardous Environment  
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## Continuous Fiber Reinforced Metal Matrix Composite Materials

906C7532A Tokyo KYOKUGEN KANKYO YO TAINETSU FUKUGO ZAIRYO in Japanese  
20 Jan 90 pp 9-24

[Article by Akira Koyama, School of Engineering, The University of Tokyo:  
"Compatibility Between Fibers and Matrices; Development of High Performance  
Intermediate Materials Manufacturing Technology; Development of Molding  
Technology<sup>(35)</sup>"]

### [Text] 1. Introduction

R&D on continuous fiber reinforced metal matrix composite materials (hereafter to be shortened as FRMs) has been promoted focusing on improved heat resistance and environmental hazard resistance properties, weak points of fiber reinforced plastics (FRP), which is sometimes required to include high specific strength and high specific rigidity in its main themes. In such cases, metal matrices are different according to their heat resistance critical temperatures, with the Al and Mg systems between 300 and 400°C. The Ti system between 500 and 600°C and Ni-group high heat-resistance alloys and intermetallic compounds at higher levels conceivable. The degree of progress in development (degree of maturity) of these materials greatly differ, which indicates a variety in their practical use<sup>(1-4)</sup>.

MITI's next-generation project has promoted the development of FRM superior in heat resistance with high specific strength as an FRM developmental strategy with a view toward industrialization. Figure 1 shows the main FRM production processes. In the research, the R&D was conducted focusing on FRMs using composite wires (infiltration wires), a high performance intermediate material, with the research roughly divided into the development of high performance intermediate materials and that of a molding method. This article mainly describes Al group FRMs developed in the next-generation project.

### 2. Compatibility Between Fibers and Matrices

In the production of FRMs, it is important to achieve the sound combination of fibers and matrix metals while suppressing the deterioration in reaction in their combination process. To this end, a production process must be designed based on the study of the compatibility between fibers and matrices. Developments are currently being carried out focusing on metallic composite materials

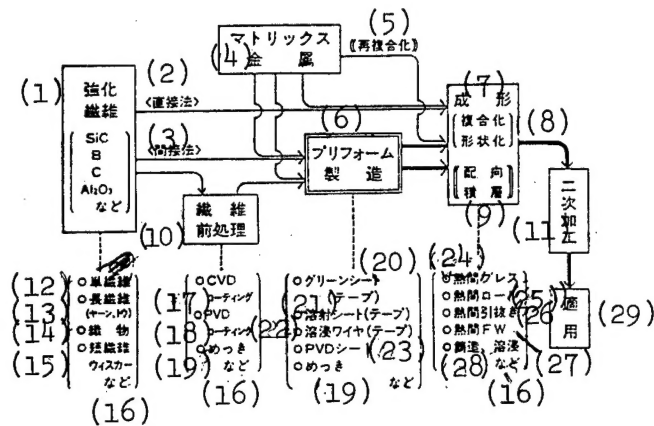


Figure 1. Main Production Processes for FRMs

Key:

1. Reinforced fibers (SiC, B, C, Al<sub>2</sub>O<sub>3</sub>, etc)
2. Direct method
3. Indirect method
4. Matrix metal
5. Recombination
6. Preform, production
7. Molding
8. Combination, shaping
9. Orientation, lamination
10. Fiber pretreatment
11. Secondary processing
12. Single fiber
13. Long fiber (yarn, tow)
14. Texture
15. Short fiber whisker
16. etc.
17. CVD coating
18. PVD coating
19. Plating
20. Green sheet (tape)
21. Spraying sheet (tape)
22. Infiltration wire (tape)
23. PVD sheet
24. Hot press
25. Hot rolling
26. Hot drawing
27. Hot FW
28. Casting, infiltration
29. Application



with aluminum as their parent material, while, with respect to FRMs in the next phase, materials are demanded which are high in specific strength and capable of withstanding at medium and high temperatures of between 500 and 600°C, higher than useful temperatures of Al and Mg. In this context, with respect to the modification of parent materials, fiber surfaces and the interface, the clarification of basic phenomena and a study of the improvement of properties were conducted so as to expect the contribution to the technical development of not only FRMs with aluminum as a parent material but also FRMs with Ti as a parent material which are likely to be important in the following step.

## 2.1. Modification of Parent Materials<sup>(5,6)</sup>

The National Research Institute for Metals systematically studied FRMs using Ti (alloy) as a parent material and CVD-system fibers as reinforced fibers as an FRM with high specific strength, expected as a material capable of withstanding medium and high temperatures of between 500 and 600°C higher than useful temperatures of Al and Mg. With FRMs of this system, materials of more than two types coexist, so they are thermodynamically in a nonequilibrium state, and interface reaction is apt to occur during high temperature molding and use of high temperature. Therefore, the modification of the parent material was studied for interface reaction control purposes.

It is necessary to obtain a clean interface in order to study interface reaction and this experiment used the PVD method to obtain single fiber composite materials by coating fibers with Ti or its alloys. The fibers were heat treated, the reaction product in the interface was identified, and its strength was measured. Based on the results, the same study was conducted with respect to massive composite materials.

The study of the single fiber composite material has found that SCS-6, a type of CVD-system SiC fibers, deteriorates least with Ti-group FRMs. The heat treatment of an FRM with pure Ti as a parent material caused TiC to be produced in the periphery of fibers and  $Ti_5Si_3$  outside them. Along with an increase in the thickness of this reaction layer, a trend of deterioration in FRM strength was observed. As additional elements to suppress interface reaction, Al, V and Mo stabilizing  $\alpha$  and  $\beta$  phases were effective, as shown in Figure 2. The effect of reaction suppression of these elements increased by adding multiple types of materials. The reaction products when alloy parent materials were used were those with TiC and  $Ti_5Si_3$  as their base, added to with the solid solution of Al, V and Mo, almost like when pure Ti was used as a parent material.

The deterioration in strength, after retaining in high temperature massive composite materials produced on the basis of the above, could be suppressed by alloying parent materials as shown in Figure 3. In other words, with pure Ti, while the strength maintenance factor after retaining it at 1123 K for  $3.6 \times 10^2$  ksec was only 60 percent, when Al and V were added, it was 70 percent, followed by 80 percent when Mo was added. It has been made clear that this deterioration is closely related to the thickness of the reaction layer but that it sometimes involves other factors.

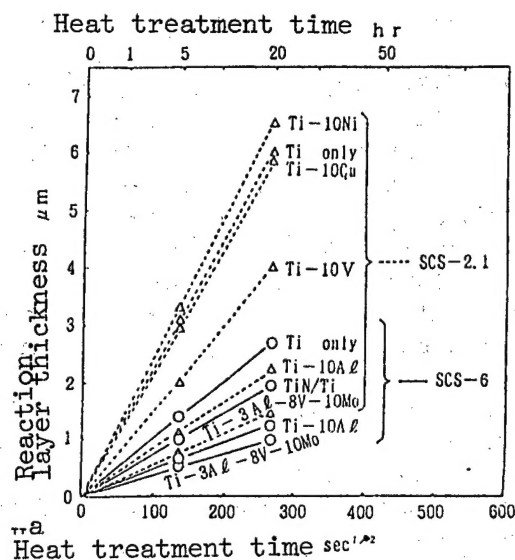


Figure 2. Changes in Reaction Layer Thickness with Heat Treatment Time for Single Fiber Composite Materials (heating temperature, 1123 K)

In other words, it has been made clear that the interface reaction between SiC fibers and a Ti matrix can be suppressed by adding Al, V and Mo to Ti and alloying them. Also, it was suggested that such a research approach would be effective for the development of FRMs with far more superior heat resistance.

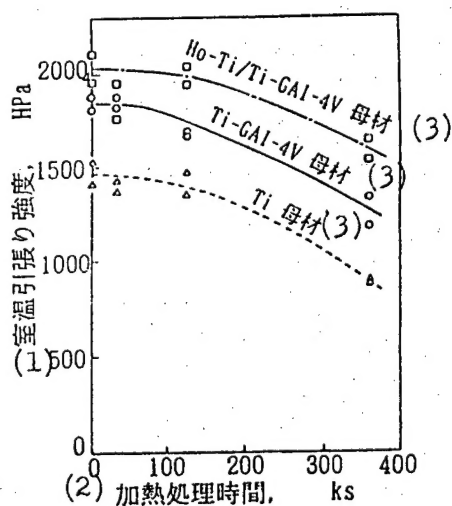


Figure 3. Changes in Room Temperature Strength with Heat Treatment Time for SCS-6/Ti(Alloy) Massive Composite Materials

Key:

1. Room temperature tensile strength
2. Heat treatment time
3. Parent material

## 2.2. Improved Fiber Coating Methods(7-10)

Carbon fibers include a PAN-system high strength fiber, a high elasticity type fiber and a liquid crystal pitch type fiber with high elastic modulus. Of these, a PAN-system high strength fiber is high in strength and priced low but disadvantageous in that it is apt to react with Al. With a view to using this fiber (TORAYCA T300) for the reinforcement of carbon fiber reinforced aluminum (C/Al), the Government Industrial Research Institute, Osaka studied the technology for providing a coat to serve as a barrier against its reaction with Al. Finally, a C/Al wire was prepared from coated fibers by Ti-B coating Al impregnation and its strength and heat resistance were examined.

With respect to barrier materials, C and ceramics (SiC, TiC and TiN) were studied. Figure 4 shows coated fiber strength. The strengths of C coated fibers are higher than those of material fibers. The strengths of fibers directly coated by ceramics are below 2/3 to 1/3 those of material fibers. However, these strengths can be improved to 90 to 80 percent of those of material fibers by the duplex coating method using C coating as a substrate. For this reason, this method was adopted for ceramics coating.

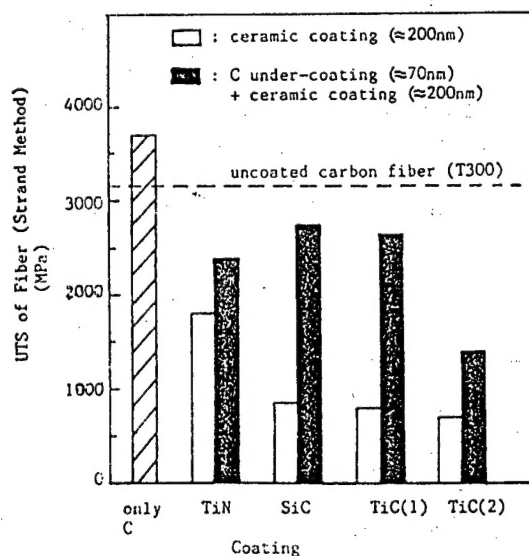


Figure 4. Strength of Ceramic Coated Carbon Fibers

The improvement in strength by the duplex coating method is attributable to the fact that cracks generated in a ceramics coat are prevented in the interface between the coat and the C coat from propagating. This is probably because the strength of the interface is relatively low. Table 1 shows the strengths of modified C/Al wires. The strengths, when preparation conditions were selected, reached 90 to 100 percent of the theoretical strength by the combination law (c: the material fiber strengths were used as the fiber strengths for theoretical strength calculation; d: the strengths of coated fibers were used). The strength of a wire prepared from carbon fibers without barrier coating was approximately 30 percent of the theoretical strength.

Coating <sup>a</sup>	Residence <sup>b</sup> time (min)	$V_f$ (%)	UTS (MPa)	Reinforcing <sup>c</sup> efficiency (%)	Strength <sup>d</sup> ROM %
C/TiN	2.4	31	950	88	87
	0.24	34	1215	107	107
C/SiC	2.4	35	1019	83	93
	0.24	32	1058	94	105
C	2.4	31	662	61	48
	0.24	40	1603	115	89

UTS of coated fibers: C/SiC, 2989 MPa; C/TiN, 3361 MPa; C, 4042 MPa.

a: Ti-B was overcoated on C/Al wire preparation.

b: 6061 alloy, 700°C; bath length 60 mm.

c: calcd. based on the strength of the uncoated carbon fiber (T300).

d: calcd. based on strengths of coated fibers.

Table 1. Changes in Strength of C/Al Wires Resulting from Residence Time in Molten Al

In order to compare the effects of barrier coating, the decrease in wire strength when contact time with molten Al was prolonged in production was examined. The decrease in strength is great with only C coated fibers, while it is minor with ceramics coated ones. Therefore, it has been concluded that sufficient effects as a barrier require not coating only C, but coating ceramics.

### 2.3. Interface Modification (11-17)

It is generally believed that the establishment of fiber surface treatment technology is indispensable in generating high performance in FRMs using ceramics fibers, such as C, SiC, etc. With PCS-system SiC fibers and PAN-system C fibers of the small-diameter multifiber type, since the advantages as FRM intermediate materials are reduced by the complexity in the production processes resulting from the surface treatment process, surface treatment was first studied. As a result, it was decided that no surface treatment be done with PCS-SiC fibers and that, with PAN-C fibers, Ti and B coating be done in order to suppress the interface reaction and to maintain wetting between fibers and matrices. The evaluation of the correlation between interface structures using composite wires manufactured in their respective test manufacturing lines and their strength properties was conducted at the University of Tokyo and the properties of intermediate materials were improved by repeating the reduction of information to the production processes. Figure 5 shows changes in research themes along with the progress in research with respect to SiC/Al. Overcoming these technical problems was the key to improving FRM strength properties.

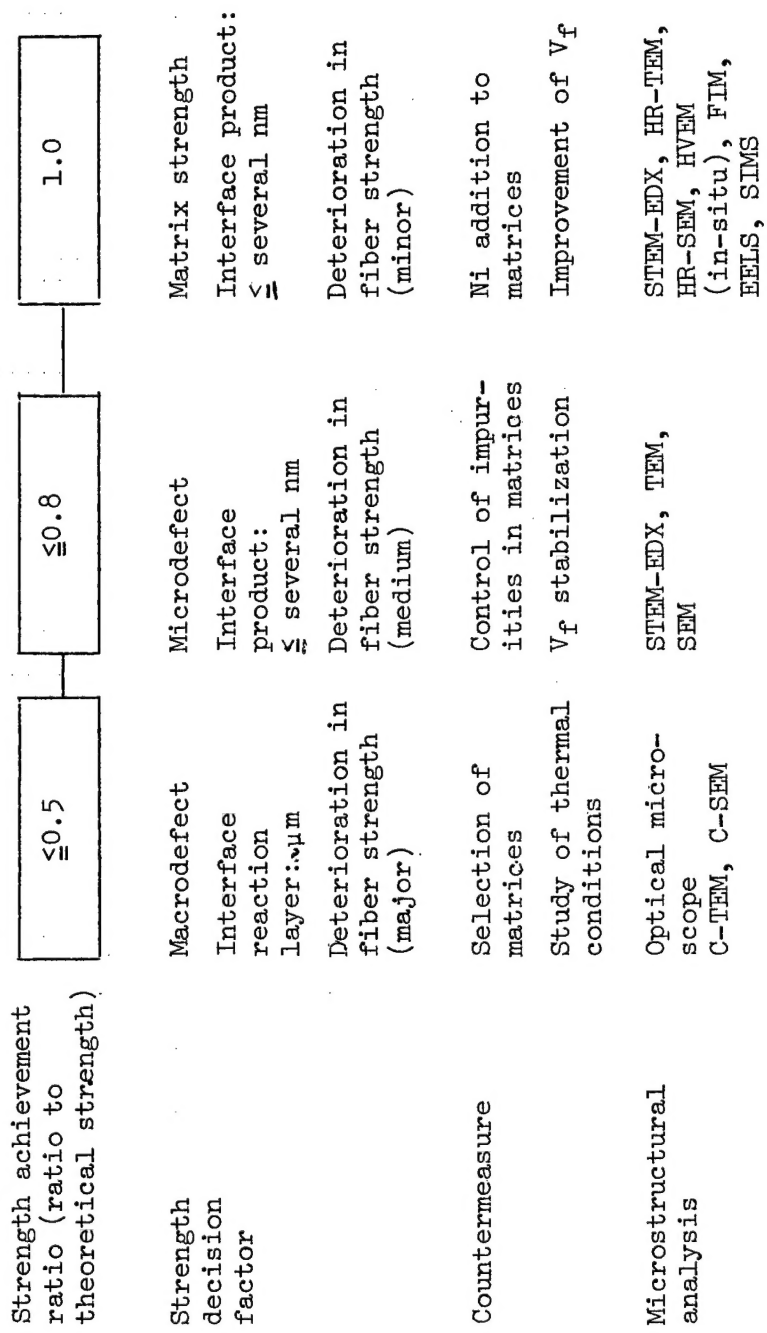


Figure 5. Changes in Research Themes Along With the Progress in Research (PCS-SiC/Al Systems)

### 2.3.1. C/Al Composite Wire

#### (1) Strength property

With the C/Al system, carbon fiber M40J-S and Al080 were used as a reinforced fiber and a matrix, respectively. M40J-S is a surface treated carbon fiber of a high elasticity type, 6000 filaments with a diameter of approximately 5  $\mu\text{m}$  forming a bundle.

The M40J-S/Al080 composite wire showed an average strength of 1.2 GPa in a tensile test with only slight fluctuation. The utilization factor of the fiber strength, however, was as low as about 60 percent, implying the presence of some factors involving strength deterioration. On the other hand, when M40-S was used as a reinforced fiber, the utilization factor was as high as about 85 percent. The great differences of M40-S from M40J-S are that M40-S is thick in fiber diameter, and 3000 filaments with a diameter of approximately 7  $\mu\text{m}$  form a bundle, which seem to result in the difference in the state of coating on fiber surfaces. In addition, as shown in the fracture observation in a tensile test stated later, the small fiber diameter results in greater influence of matrix defects including pores. As a result of a tensile test of heat treated specimens, an average tensile strength of 1.6 GPa was obtained. On the other hand, as shown in Table 2, tensile strengths of both carbon fibers extracted from specimens which had undergone heat treatment and those which had not were approximately 3.2 GPa and no difference between the two could be observed in Weibull analysis results. This implies that an increase in strength by heat treatment results from the matrix or the interface. Also, the theoretical strength calculated by the simple combination law using these results is in good accordance with the tensile test results of the heat treated specimens, and it is guessed that the specimens have no factors to decrease strength other than thermal deterioration of fibers in the production processes. This implies that the thorough prevention of thermal deterioration of fibers is necessary in order to improve performance of J40J-S/Al080 composite wires.

Table 2. C/Al Composite Wire and C Fiber Tensile Test Results

	Wire Strength (GPa)	Fiber Strength (GPa)	Weibull Factor
Preheat treatment	1.2	3.2	5.0
Postheat treatment	1.6	3.2	4.5

#### (2) Microstructure

Figure 6 (not reproduced) shows an example of a fiber-matrix interface structure, in which needle-like and massive products can be observed on the fiber surface. The needle-like products were identified with  $\text{Al}_4\text{C}_3$  by means of electron beam diffraction pattern analysis, etc. Figure 7 (not reproduced) shows the state of dislocation around interface products and it is found that integrated dislocation has occurred in the periphery of interface products. This implies that interface products can be a source of concentrated stresses, which causes the material to fracture with ease and result in early fracture of fibers within composite materials and separation of fibers and matrix when

load is applied to a material and a level of a stress generated becomes higher, leading to a decrease in material strength. It was shown that with the C/Al system, the reaction between fibers and matrices via CVD coating layers of Ti and B was an important factor to determine strength properties. Also, it was anticipated that the formation of micropores between fibers had great influence on strength.

### 2.3.2. PCS-SiC/Al Composite Wire

#### (1) Strength properties

With the PCS-SiC/Al systems, PCS-system SiC fibers were used as reinforced fibers and pure Al and an alloy with 0.9 to 7.2 wt% Ni added to pure Al used as matrices. PCS-system SiC fibers have an average diameter of 13  $\mu\text{m}$ , 250 filaments forming a bundle.

Applying the method for improving  $V_f$  in which pure Al was successfully used as a matrix, PCS-SiC/Al-Ni composite wires were manufactured. As a result, the improvement in tensile strength resulting from Ni addition was identified, which seemed to be partially caused by the generation of an Al/Al<sub>3</sub>Ni eutectic phase as a result of X-ray diffraction measurement. Figure 8 presents the dependence of tensile strength of SiC/Al-Ni composite wires on Ni content.

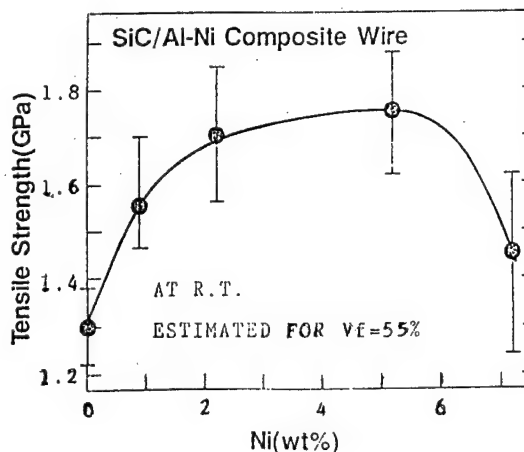


Figure 8. Dependence of Tensile Strength of SiC/Al-Ni Composite Wires on Ni Content

Tensile strength shows a peak around Ni addition of 5 wt%, while it has also been found that less addition results in an effect to some extent. This trend similarly appeared in the result of a 723-K tensile test, thereby showing that Ni addition was effective means of improving strength properties at room temperature and high temperature. On the other hand, from the tensile test results with PCS-SiC fibers. It was found that an increase in strength and Young's modulus could be confirmed. This implied that Ni diffusion from matrices caused strength properties of fibers to increase, leading to the anticipation of the mechanisms of changes in fiber microstructures and interface structures.



## (2) Microstructures

Figure 9 (a) and (b) (not reproduced) show microstructures of a PCS-SiC/Al-5.2% Ni composite wire and the fiber-matrix interface of a PCS-SiC/Al composite material, respectively. PCS-system SiC fibers are sintered at a temperature enabling the highest strength to be obtained and it is considered that their structure is in a phase where extremely fine crystallites crystallize from the amorphous state. With PCS-SiC/Al-5.2% Ni, the analysis of electron beam diffraction figures found that microcrystallization was being promoted. This seems to cause the abovementioned increase in strength and Young's modulus of fibers. An increase in strength and Young's modulus caused by the microcrystallization of fibers is in good accordance with the results of neutron irradiation research, thereby implying the feasibility of improving strength properties of PCS-system SiC fibers, showing the thermally highest strength. In the similar heat history within a pure Al matrix, however, the deterioration in strength was caused, thereby implying the importance of Ni diffusion from the matrix or that of the slight difference in heat history. While it had been accepted that PCS-SiC/Al composite materials met the theoretical strength calculated using strengths of fibers and the matrix with good interfaces, no interface microcrystals which were observed with PCS-SiC/Al could be observed with respect to PCS-SiC/Al-5.2% Ni composite materials and it was made clear that they possess better interfaces than PCS-SiC/Al counterparts.

## 3. Development of High-Performance Intermediate Materials Manufacturing Technology

The improvement of the performance of C/Al and PCS-SiC/Al composite wires is a critical problem since their performance will be a critical factor to decide mechanical properties of moldings. In this context, R&D on materials produced by molten metal impregnation has been promoted by feedbacking results of strength properties evaluation and microstructure analysis to the test manufacturing line.

With PAN-system C/Al, a study was promoted with respect to the degree of graphitization of fibers, the difference in their surface treatment and their compatibility with matrix Al alloys. As a result, it has been found that an optimum combination is high-elasticity type carbon fibers and a pure Al matrix.

Also with PCS-system-SiC/Al, a study of its compatibility with matrix Al alloys was made, particularly focusing on the analysis of interface microstructures with the result that the theoretical strength was achieved with the system having pure Al as a matrix. After that, the addition of an alloying element was studied in order to improve high temperature properties of matrices and wire added by Ni were test manufactured. On the other hand, the establishment of basic technology was promoted for manufacturing by vacuum low-pressure thermal decomposition of PITCH-system C/Al likely to be applied to composite wires capable of use at higher temperatures.

### 3.1. PAN-System Carbon Fiber/Aluminum Composite Wires (18-24)

With respect to carbon fiber-system intermediate materials, research intended to establish manufacturing technology and to achieve high performance was



conducted in order to obtain high-performance composite wires utilizing superior dynamical properties of PAN-system carbon fibers, based on CVD and infiltration.

The important technical problems for developing high-performance composite wires can be summarized into two points--the improvement in the wettability of carbon fibers and aluminum and the prevention of fiber deterioration caused by the reaction between the above two. The expertise to overcome this antinomy relationship is the key to success.

With respect to the improvement of the wettability, the research was promoted on the technology for continuously forming coating by CVD on surfaces of 3000 to 6000 filaments comprising a carbon fiber bundle. As a result, it was found that a mixture of Ti and B which had not formed compounds, such as  $TiB_2$  and  $TiC$ , was the most desirable as a coating material for improving the wettability and that retaining either linkage on carbon fiber surfaces (pretreatment) prior to CVD, by heat treating, carbon fibers to which a sizing agent attached could lead to stabilized wetting. Based on this, an original technique for stably manufacturing composite wires was established. Figure 10 presents a schematic diagram of the C/Al composite wire manufacturing process. On the other hand, research on the improvement of the compatibility between carbon fibers and matrix was promoted in order to improve performance of composite wires. With regard to reaction, success was achieved in suppressing the reaction between the two within a scope in which the composite wire's manufacturing rate was not forced to reduce very much by controlling sintering temperature for carbon fibers and their surface treatment. This was done after quantitatively making clear the degree of graphitization of carbon fibers and the reactivity between carbon fibers and matrix.

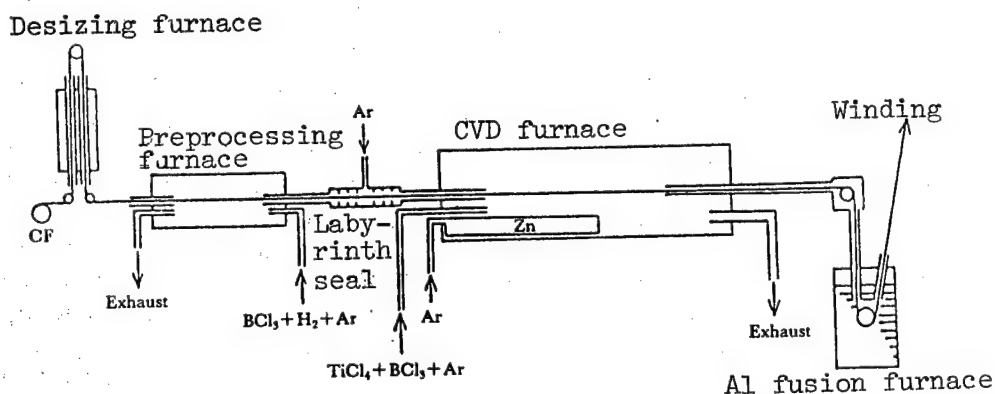


Figure 10. Wire Preform Test Unit (Postmodification)

In addition, as for an approach from the matrix side, research was conducted on the influence of the composition of aluminum alloys on the composite wire strength. As a result, it was made clear that, as shown in Figure 11, Si, Mg and Cu contained in matrix had a bad effect on the composite wire strength, irrespective of the above reaction, thereby finding, that of aluminum alloys, JIS Al080 was suitable as a matrix.

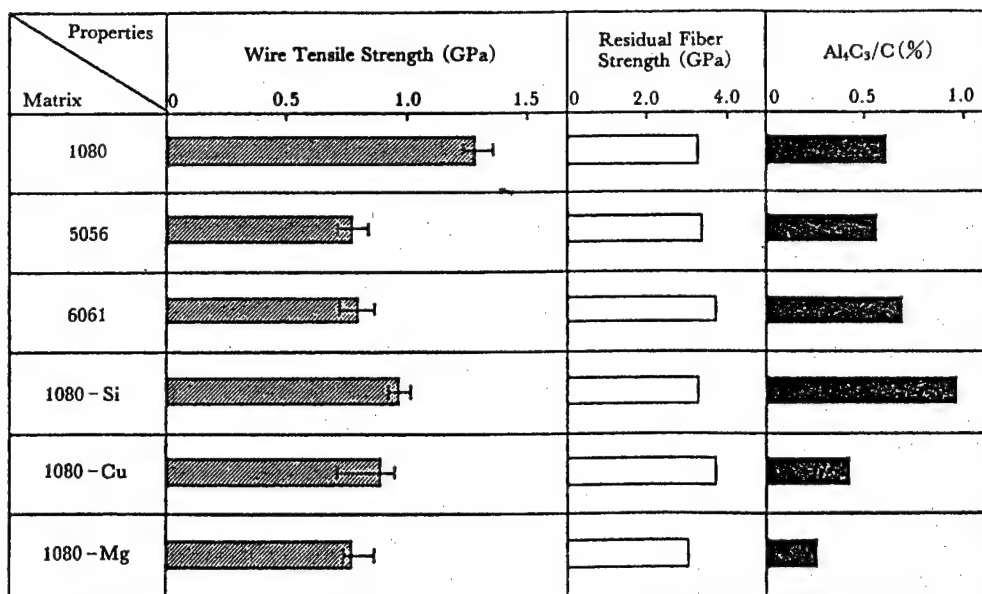


Figure 11. Influence of Matrix Composition on Wire Preform Strength

Based on such research results, Kyono, et al, finally developed M40J/1080, a high-strength composite wire combining "Toreka [phonetic]" M40J, a PAN-system carbon fiber with high strength and high elastic modulus, and Al080 and established the basic technology for its stable manufacturing. The composite wire developed, as shown in Figure 12, retained tensile temperature at room temperature until the temperature reached 723 K, thereby achieving the developmental target value at this temperature of 1320 MPa.

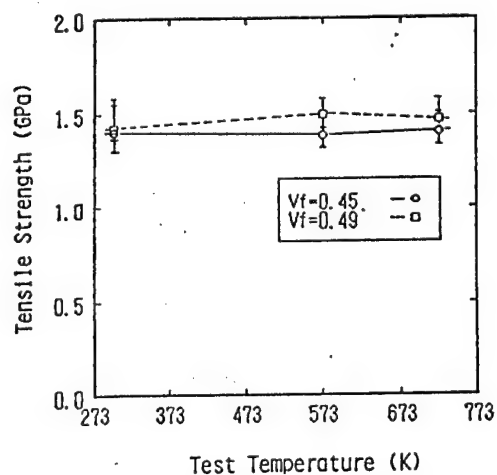


Figure 12. Temperature Dependency of M40J/1080 Wire Preform Tensile Strength

### 3.2 Pitch-System Carbon Fiber/Aluminum Composite Wires (25-29)

Suzuki, et al, conducted research targeting the production of pitch-system carbon fiber/Al composite wires by uniformly and closely penetrating matrix Al into a carbon fiber bundle, without causing fiber deterioration, by vacuum low-temperature thermal decomposition using organic Al. A systematic study was carried out with respect to the gasification temperature of triisobutyl Al( $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ), deposition temperature and pressure of Al, the type, flow and gas blasting direction of a carrier gas. Based on the results, a device for continuously manufacturing pitch-system carbon fiber/Al wires (Figure 13) was designed and test manufactured. This was followed by a study of the influence of fiber travel speed (Figure 14) and energization heating and performance comparisons using various pitch-system carbon films. The significance of this technology can be summarized as follows.

(a) Technology for homogeneous chemical vapor impregnation of Al into fiber bundles was established, making use of the superior characteristic of CVD and a method for producing intermediate materials with high fiber content was developed.

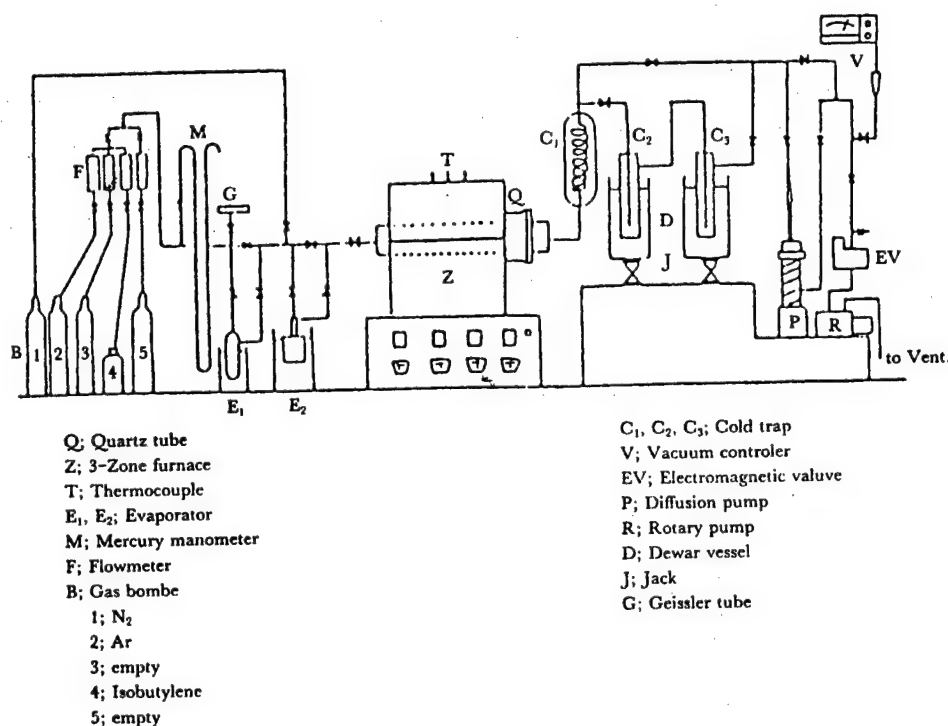


Figure 13. Schematic Diagram of the Unit

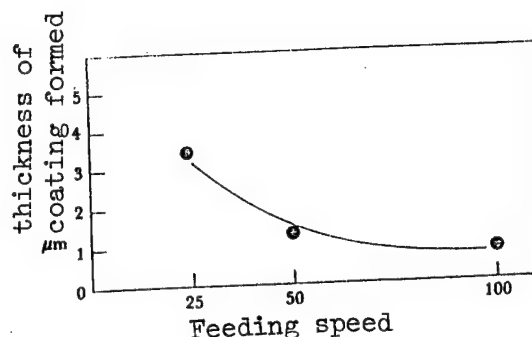


Figure 14. Relationship Between Al Thickness and Fiber Feeding Speed

(b) It was made clear that pitch-system carbon fibers are weak in reactivity with Al due to their surface crystal structures, and suitable for reinforced fibers.

(c) A method was established for manufacturing intermediate materials at temperature below its melting point by using an organic metal as a material.

(d) It was suggested that this technology could be applied to other metal matrices (Ti, Mg) and that, in particular, it would serve to create inter-metallic compound matrix FRMs catching attention as an advanced material superior in heat resistance to Al matrix FRMs.

The remaining problems include the improvement of fiber bundle opening technology, the reduction in production cost and the establishment of the anti-oxidation coating treatment for intermediate materials obtained.

In addition, the interdependence between the elastic modulus of pitch-system carbon fibers and the strength for an intermediate material (Figure 15) was found and the following knowledge was obtained.

(a) The higher the elastic modulus, the lower the postcoating tensile strength.

(b) The tensile strength of an Al coated fiber after heating to 773 K (500°C) increases with the coal pitch system, while it decreases with the petroleum pitch system.

In other words, it was suggested that, when Al is reinforced by pitch-system carbon fibers, it is important to select the proper system since the elastic modulus optimum for pitch-system carbon fibers to be used exists and the effectiveness of the basic technology was demonstrated.

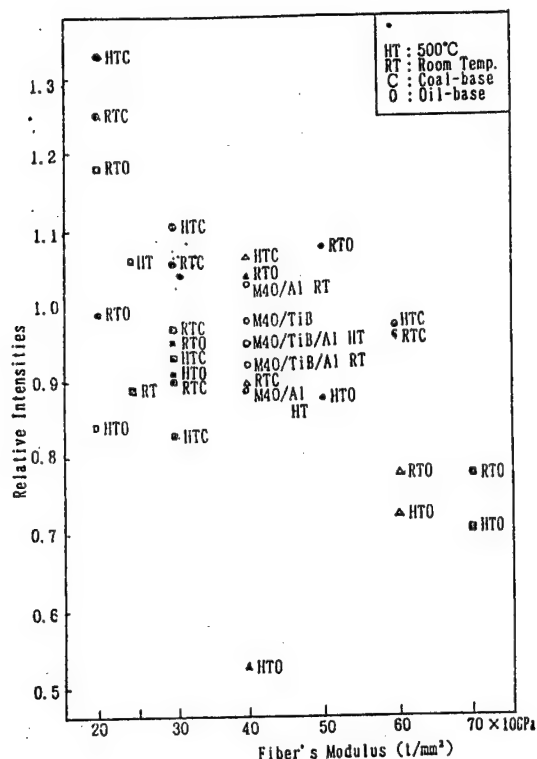


Figure 15. Relationship Between Relative Tensile Strength Values and Fiber Elastic Modulus of Al Coated Pitch-System Carbon Fibers (room temperature, 500°C)

### 3.3. SiC Fiber/Al Composite Wires(30-34)

The important technical problem in developing high-performance composite wires was to produce sound ones without coating ceramics on fibers and, at the same time, to establish production technology for continuously manufacturing products with stable properties at the test manufacturing plant. Figure 16 illustrates the outline of composite wire manufacturing processes. In these processes the optimization of an intermediate material considering the molding process was carried out.

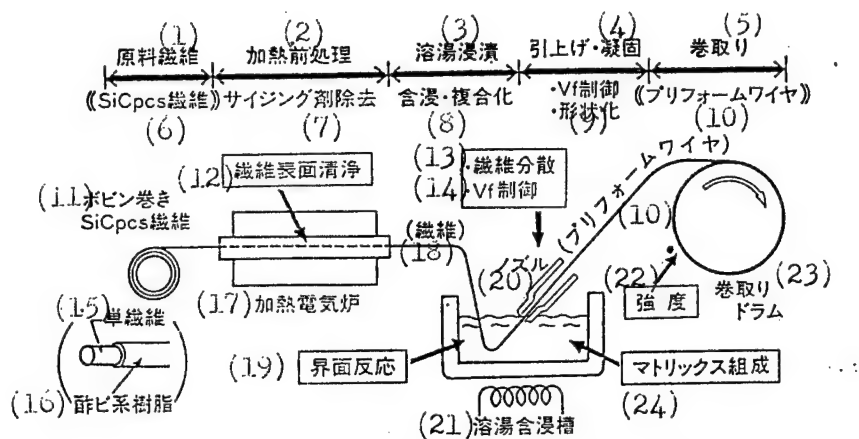


Figure 16. PCS-SiC/Al-System Preform Wire Production Processes

Key:

1. Material fiber
2. Heating pretreatment
3. Molten metal dipping
4. Lifting, solidification
5. Winding
6. SiC<sub>pcs</sub> fiber
7. Removal of sizing agent
8. Impregnation, combination
9. V<sub>f</sub> control, shaping
10. Preform wire
11. Bobin wound SiC<sub>pcs</sub> fiber
12. Fiber surface cleaning
13. Fiber dispersion
14. V<sub>f</sub> control
15. Single fiber
16. Vinyl acetate resin
17. Heating electric furnace
18. Fiber
19. Interface reaction
20. Nozzle
21. Molten metal impregnation tank
22. Strength
23. Winding drum
24. Matrix composition.

(a) Figure 17 presents an increase in wire strength along with the progress in research, showing the establishment of technology for manufacturing materials with few defects, by reducing to the farthest, the deterioration of fibers in manufacturing processes.

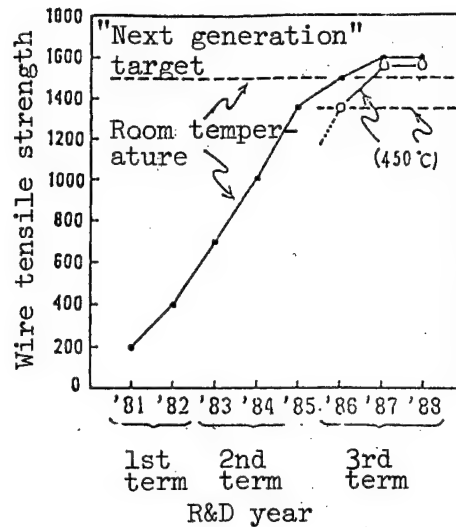


Figure 17. Development of Nikalon [phonetic]/Al Wire Preform

(b) The tensile strength of a preform wire obtained is a high value according to the theoretical law; a higher level compared to short fiber/whisker/particle reinforced composite materials as well as Al alloys and Ti alloys. Also, it was found that the saturation value was related to the improvement in wire strength and with the increase in fiber volume percentage. It was studied to make use of small-diameter fibers in order to improve the saturation value (Figure 18), resulting in improved  $V_f$  and strength of wires.

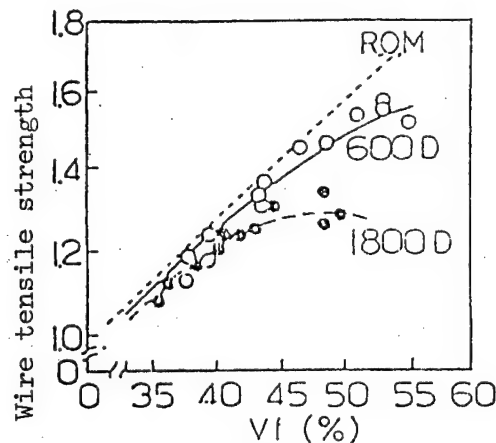


Figure 18.  $V_f$  and Wire Tensile Strength

It was also studied to adopt an Al-Ni eutectic alloy with high high-temperature strength in order to limit the decrease in strength at high temperature in case of adopting pure aluminum matrices. Figure 19 presents the temperature dependency of wire strength, showing that the adoption of an Al-Ni matrix enables high-temperature strength to be stabilized. It has been found that this material has eutectic texture with Al- $Al_3Ni$  matrix, with superior

properties by means of double reinforcement, fiber reinforcement by the eutectic

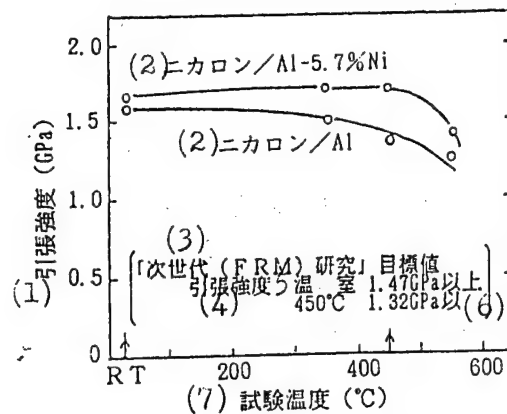


Figure 19. Wire Strength at Room Temperature and High Temperature (Al-5.7 wt% Ni system, pure Al system)

Key:

- |  |                     |
|--|---------------------|
| 1. Tensile strength                              | 6. Above 1.47 GPa,  |
| 2. Nikalon [phonetic]                            | above 1.32 GPa      |
| 3. "Next generation (FRM) research" target value | 7. Test temperature |
| 4. Tensile strength                              |                     |
| 5. Room temperature                              |                     |

phase and that by SiC fibers. Also, it is important that a decrease in molten metal temperature, in the course of wire production, is effective for maintaining fiber strength. Figure 20 presents rotary bending properties of FRMs molded from a PCS-SiC/Al composite wire and the result of its salt water corrosion test, showing these properties to be extremely superior to those of existing materials.

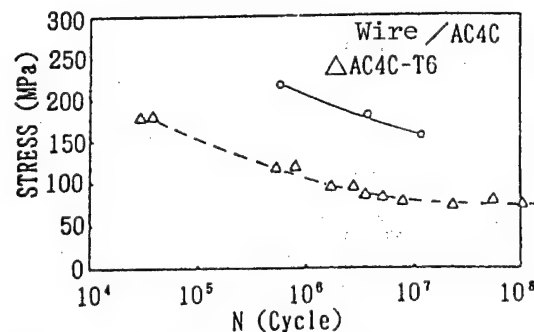


Figure 20. Rotary Bending Properties of Wire Preform Applied FRMs (unidirectional materials)



#### 4. Development of Molding Technology<sup>(35)</sup>

The fundamentals of FRM molding processes are heating and pressurizing and, since materials are handled at high temperature, it is important to optimize processes compatible with controlling the interface reaction between fibers and matrices and achieving sound combination and molding. When an intermediate material is used, it is essential to develop materials coordinated to molding processes, and it has been made clear that it is necessary to carry out the integrated optimization covering from material design to process design to application development.

Table 3 shows the representative molding processes developed in the next-generation project. With molding using composite wires, a study was made focusing on hot press and hot rolling<sup>(36-39)</sup>, and, as a thin wall molding process aimed for the application to space structures, laser roll molding was developed<sup>(40-42)</sup>. In addition to materials making use of CVD fibers, processes related to high temperature dynamic properties and matrix alloy composition were developed<sup>(43-45)</sup>. While with HIP molding, a method using metallic powder of Al and Ti matrices was developed, thereby succeeding in near net shape molding and improving degrees of freedom of matrix composition<sup>(46, 47)</sup>. With molding of the SiC whisker/Al system, squeeze cast extrusion molding was adopted, thereby succeeding in molding a material with 1-GPa class high strength by improving matrix composition and by controlling microdefects by liquid phase HIP processing of billets<sup>(48, 49)</sup>.

Table 3. Representative Molding Processes Developed in the Next Generation Project

Typical	Material System	Fabrication Process	
		Preform	Consolidation Method
C/Al	M40J/1080	wire	hot pressing
	M40J/1080	wire	hot rolling
	M40J/1080	wire	laser heating and rolling
	M40/6061	green sheet	liquid phase pressing
	M40J/1080	wire	HIP
	UHM/4032	powder slurry	
SiC/Al	Nicalon/1050	wire	hot rolling
	Nicalon/1050	wire	hot pressing
	Nicalon/1050	wire	HIP
	Nicalon/1050	wire	laser heating and rolling
	SCS-2/6061	green sheet	hot pressing
	SCS-2/Al4Ti	LPP spray sheet	
SiC/Ti	SCS-6/Ti6Al4V	green sheet	hot pressing
	Ti15V3Cr3Al3Sn	fiber/powder sheet	HIP
	SCS-6/Ti6Al4V		
SiC	Ti6Al2Sn4Zr6Mo	green	squeeze casting and hot extrusion
	Ti15Mo5Zr3Al		
SiC	whisker/Al	green	

The following are descriptions of dynamic properties of FRMs obtained by various molding methods. Figure 21 presents the relationship between specific strength and specific elastic modulus. The values in the figure indicate properties of one-way reinforced materials in direction of  $0^\circ$ , showing that superior properties have been obtained, compared to general structural metallic materials, although it may not be proper to compare.

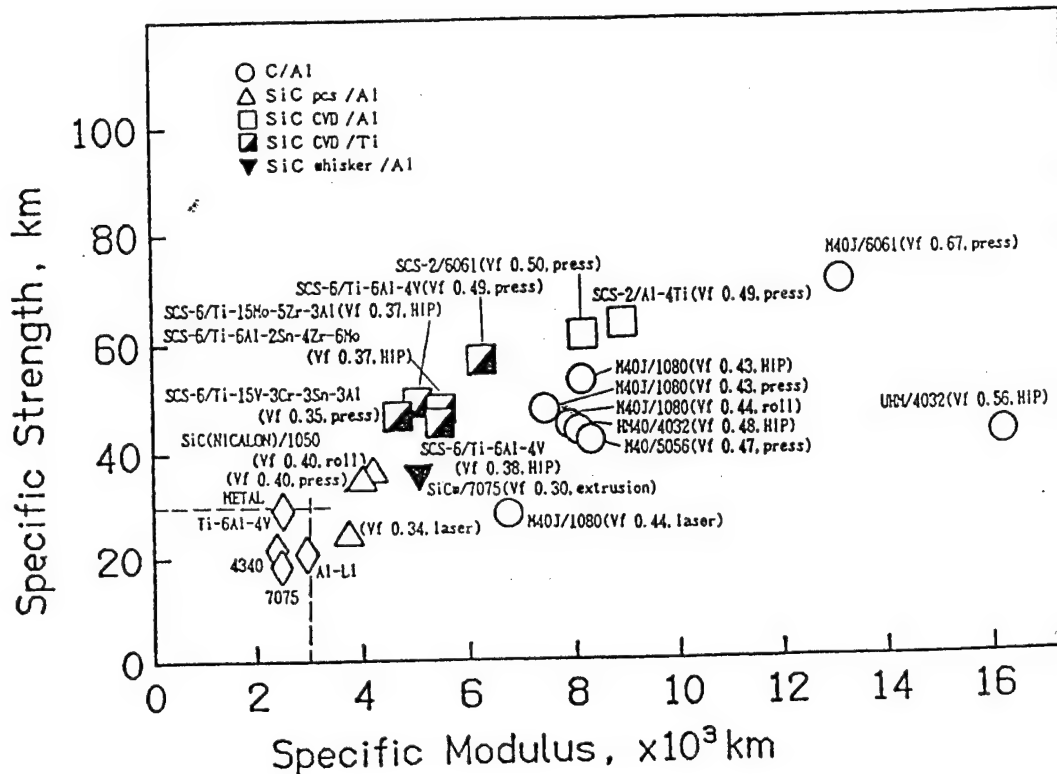


Figure 21. Relationship Between Specific Strength and Specific Elastic Modulus of Various Metallic Radical Composite Materials

Figures 22 and 23 present high temperature strength properties of FRMs, showing the great improvement in heat resistance resulting from combination with both Al and Ti. With CVD-SiC/Al-Ti and Al-8Cr-1Fe, in particular, high temperature strength, similar to Ti matrix, has been obtained. Creep fracture properties (Figure 24) are superior to INCOLOY800 at  $600^\circ\text{C}$ , showing superior property of about 1.5-fold that of INCONEL781 with respect to specific creep fracture strength. Compressive strength was strongly dependent on reinforced fiber properties and, as shown in Figure 25, CVD-SiC was particularly strong, and, with small diameter multifibers, PCS-SiC was found to possess superior properties. Figures 26 and 27 present the reinforcing direction dependency of dynamic property values of one-way reinforced materials, making clear that these properties greatly decrease in direction perpendicular to fibers. However, PCS-SiC/Al with high strength of the interface between fibers and the matrix shows a smaller decrease in strength than PAN-C/Al, which has low interface strength in direction perpendicular to fibers, showing that the

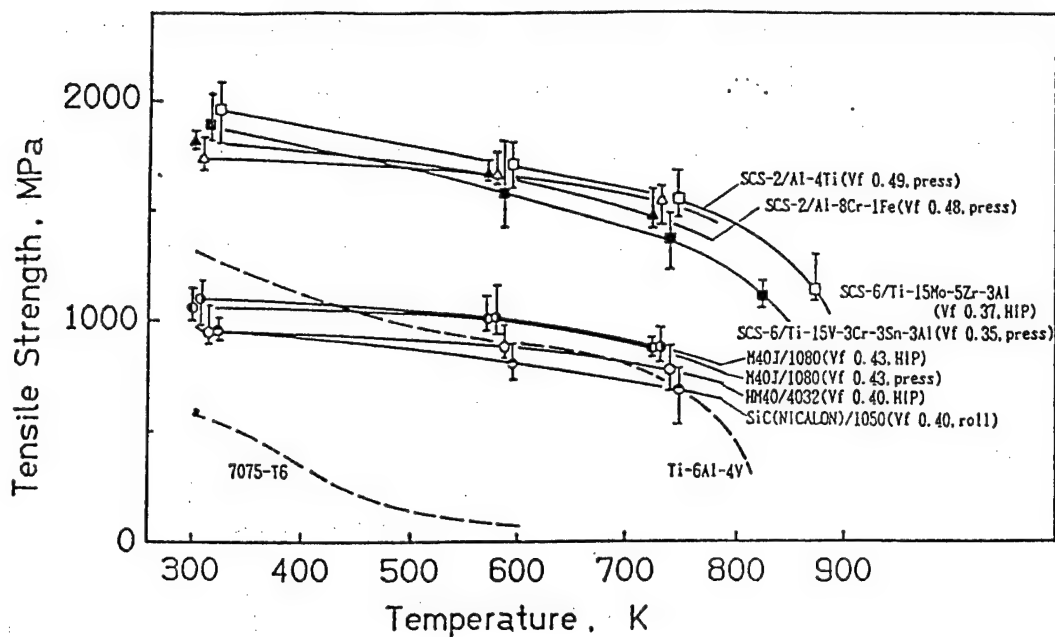


Figure 22. Temperature Dependency of Tensile Strength of Various Metallic Radical Composite Materials

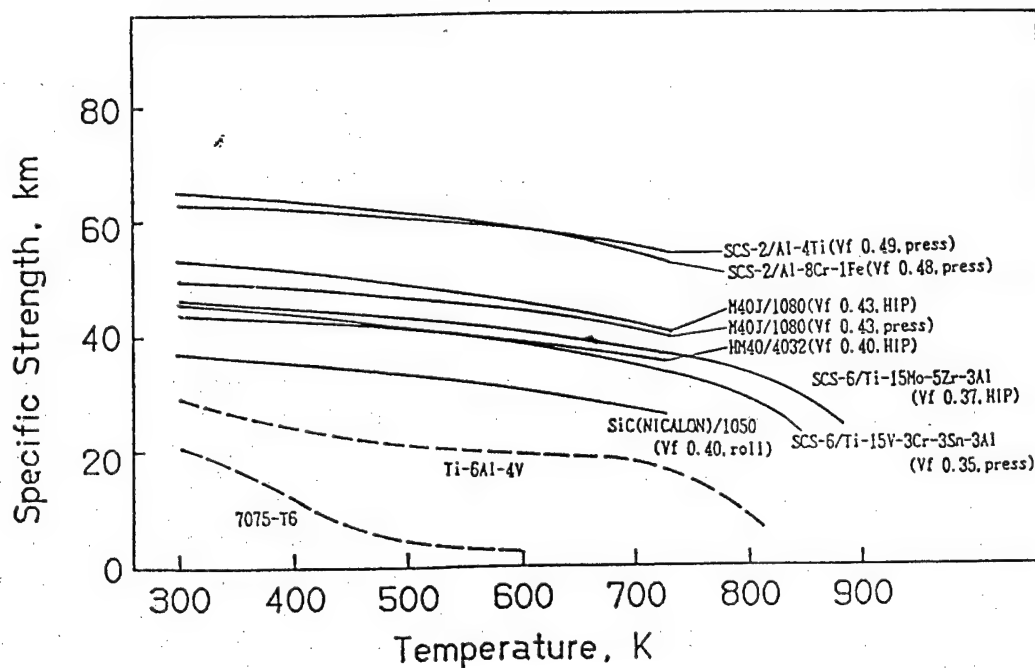


Figure 23. Temperature Dependency of Specific Strength of Various Metallic Radical Composite Materials

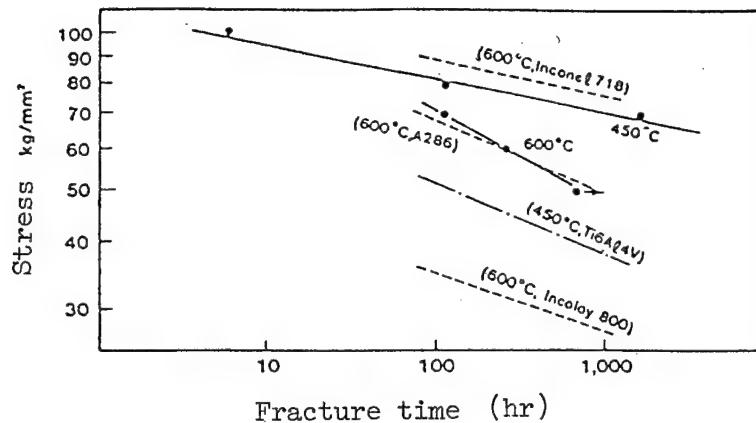


Figure 24. Creep Fracture Strength of SCS-6/Ti-15Mo-5Zr-3Al

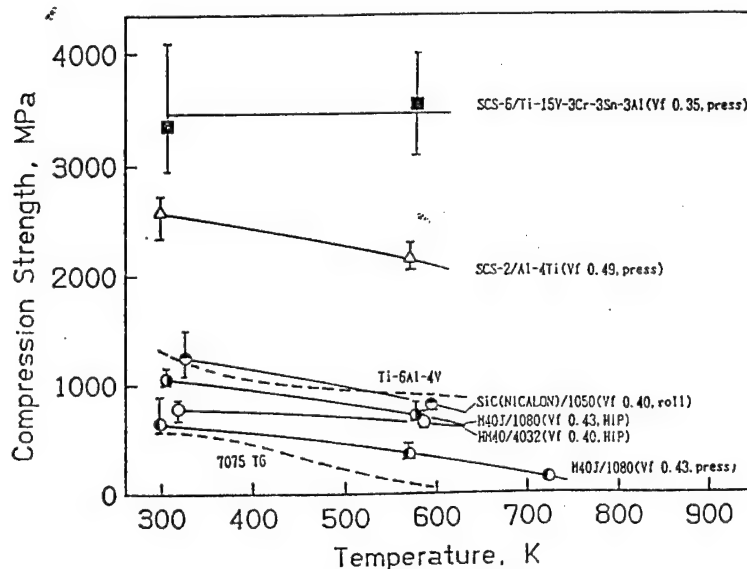


Figure 25. Temperature Dependency of Compressive Strength of Various Metallic Radical Composite Materials

concept of interface construction between the two is basically different. Figure 28 presents an example of fatigue properties of Al-group FRMs. These fatigue properties are superior to conventional Al alloys. Figure 29 presents normalized results of Al and Ti matrices. These matrices are roughly divided into ones whose S-N curves were close to those of ordinary metallic materials, ones whose S-N curves were close to horizontal in gradient and ones located between the two. S-N curves depended on the state of bonding of the interface, the greater the bonding strength, the more perpendicular, to load direction accompanying fiber fracture, the progress in cracks, and the gradients of S-N curves became great and fatigue limit ratios showed small values. In addition to the above, Charpy properties and acoustic wave properties have been evaluated using various moldings, which are omitted here due to shortage of space.

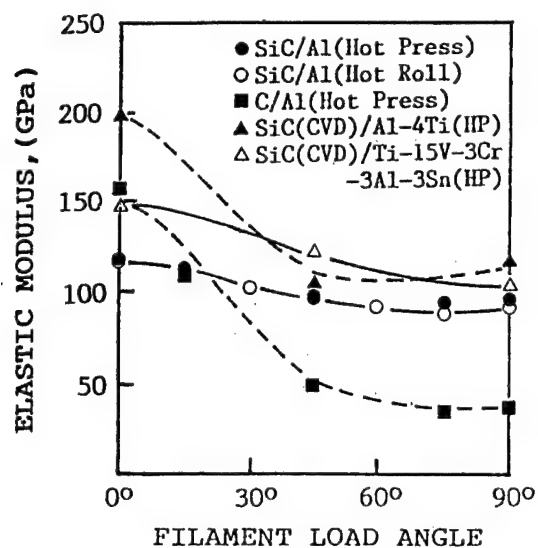


Figure 26. Reinforced Fiber Directional Dependency of Elastic Modulus

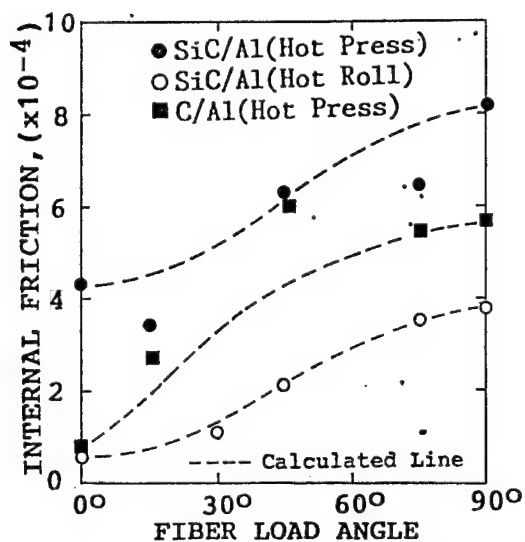


Figure 27. Reinforced Fiber Directional Dependency at Room Temperature of Internal Friction ( $Q^{-1}$ )

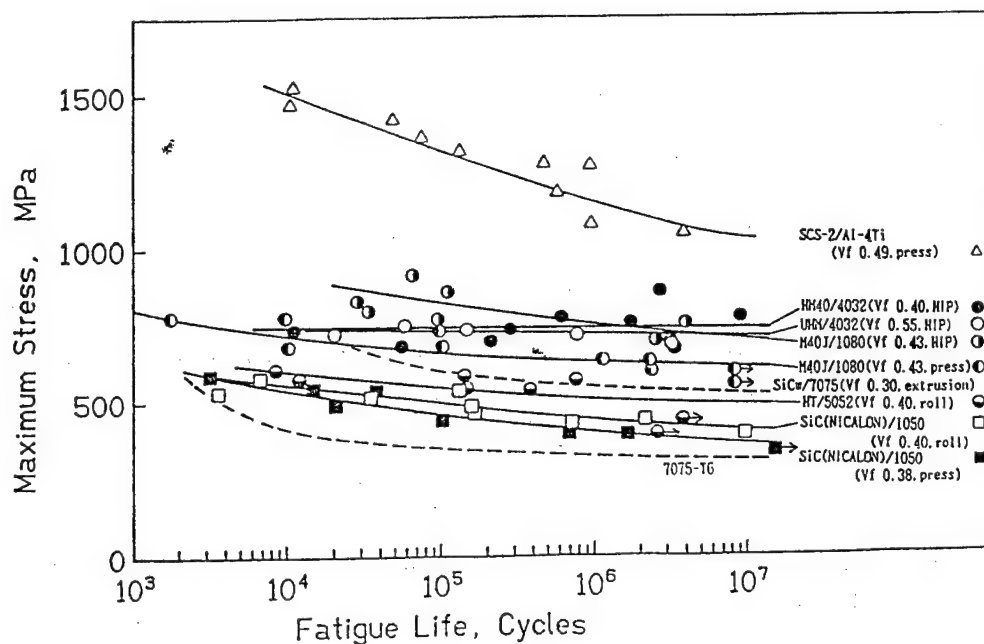


Figure 28. Fatigue Life of Al Radical Composite Materials (RT,  $R \sim 0.1$ )

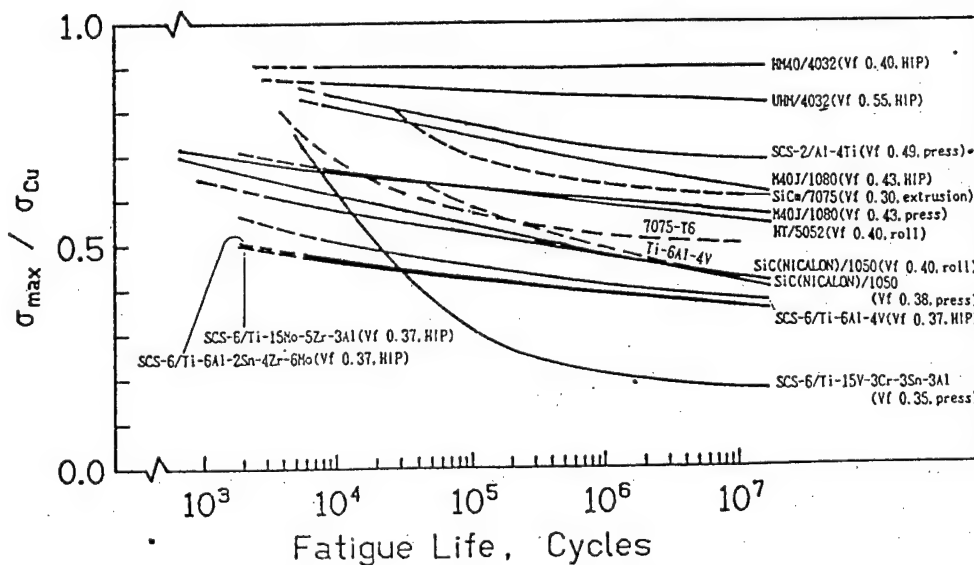


Figure 29. Normalized S-N Curves of Various Metallic Radical Composite Materials

## 5. Conclusion

Remarkable progress has recently been made in the development of FRMs but there is a long way to go to their practical use, when compared to FRPs. However, Al matrix FRMs described in this article have substantially approached their practical application and it is anticipated that Al radical FRMs will lead

environment hazard-resistant/heat resistant composite materials in the future. It is also expected that the development of FRMs withstandable to higher temperatures will make steady progress in the implementation of the high environmental hazard-resistant advanced composite materials development project, etc. In this context, it is desired that circumstances will be readjusted so as to actively develop materials aimed for use in every aspect of the environment led by the energy sector, such as space, air navigation, atomic energy and nuclear fusion. Also, with respect to the evaluation of the irradiation environment which is the most important of all environmental factors and entails difficulties in research. Research using various accelerating particles and neutrons has been promoted with insufficient results and is also considered necessary to readjust the research environment in this regard.

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## Whisker Reinforced Alloys

906C7532B Tokyo KYOKUGEN KANKYO YO TAINETSU FUKUGO ZAIRYO in Japanese  
20 Jan 90 pp 25-35

[Article by Hideharu Fukunaga, School of Engineering, Hiroshima University:  
"Types and Properties of Mass Produced Whiskers; Process; Heat Resistance and  
High Temperature Strength; Working Temperature Limit and Its Improvement;  
Application of Whisker Reinforced Alloys"]

### [Text] 1. Introduction

Being slender needle crystals with extremely high strength, a metallic ceramic whisker has become important as a reinforced fiber of composite materials. Particularly, since SiC whiskers came to be mass produced from rice hulls in the United States in 1978, and since titanate acid, potassium whiskers and SiC whiskers came to be industrially produced in succession in Japan around 1979. Progress has been made in research on whisker reinforced alloys (a type of MMC) produced by reinforcing Al alloys, etc. using these whiskers as industrial materials. The history of whisker reinforced alloys is slightly less than a decade but the expectation as a new material has remarkably promoted the research on them, thereby relatively establishing themselves as a material. In recent years, they have been put to practical use as a functional material for parts for use in special environment, such as machines operating at medium and high temperatures, space and radiation. This article describes their manufacturing, current properties, limit of heat resistance and the concept of their practical use.

### 2. Type and Properties of Mass Produced Whiskers

A whisker is a needle crystal grown into an extra fine fiber 0.1 to 2  $\mu\text{m}$  thick and 20 to 100  $\mu\text{m}$  long, looking like powder to naked eyes. Research on whiskers themselves is not new and graphite whiskers, diamond whiskers and various metallic and ceramic whiskers can be grown today on a laboratory basis. Of them, those industrially usable are, as shown in Table 1, SiC,  $\text{Si}_3\text{N}_4$ ,  $\text{K}_2\text{O} \cdot 6\text{TiO}_2$ ,  $9\text{Al}_2\text{O}_3$ ,  $2\text{B}_2\text{O}_3$  and ZnO and  $\text{Al}_2\text{O}_3$  and  $\text{TiB}_2$  whiskers. These are expected to be on the market shortly.

SEM observation of these whiskers finds that they are in the state of fiber with aspect ratios of 20 to 200 as shown in Figure 1 (not reproduced). Only

ZnO whiskers, however, have grown into tetrapot [phonetic]-shaped unique shapes as shown in Figure 2 (not reproduced). Whiskers greatly feature mechanical strength close to that of ideal crystals. They generally have few defects because their growth is due to few internal defects resulting from their growth configuration. Ceramics whiskers, light in specific gravity and superior in heat resistance, are utilized for reinforcing metals such as Al alloys. Whiskers actually produced seem to disperse in diameter, for example, from 0.2 to 2  $\mu\text{m}$ , and, along with this, to disperse in strength from close to

Table 1. Types and Properties of Mass Produced Inorganic Whiskers

1	2	3	4	5	6	7	8	9	10	11	12	13
ウィスカー	相	直径 ( $\mu\text{m}$ )	長さ ( $\mu\text{m}$ )	比重 ( $\text{g}/\text{cm}^3$ )	比熱 ( $\text{kcal}/\text{kg}^\circ\text{C}$ )	熱伝導率 ( $\text{kcal}/\text{m}^\circ\text{C}$ )	線膨張係数 ( $1/^\circ\text{C}$ )	耐熱温度 ( $^\circ\text{C}$ )	引張強さ ( $\text{GPa}$ )	弾性率 ( $\text{GPa}$ )	かたさ ( $\text{HV}$ )	成分 (%)
SiC (東海 カーボン)	$\beta$ -SiC	0.1-1.0	50-200	3.2			$4.5 \times 10^{-6}$	1600	2.9-13.7	392-686	>9 HV2800	20 SiC > 98 SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> 痕跡
SiC (タテホ 化学)	$\beta$ -SiC	0.05-0.2	10-40	3.2	0.24	0.9 (600-1200 $^\circ\text{C}$ )	$4.4 \times 10^{-6}$ - $4.7 \times 10^{-6}$	350 (酸化温度) 2550 (分解温度)	20.6	480	13 (新E-7)	24 SiC > 98 Mg < 0.25 Ca < 0.38 Al < 0.06 Fe < 0.501
Si <sub>3</sub> N <sub>4</sub> (タテホ 化学)	$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	0.1-1.6	50-300	3.2	25 0.17 (常温) 0.30 (1000 $^\circ\text{C}$ )	0.6 (200 $^\circ\text{C}$ ) ~0.5 (1000 $^\circ\text{C}$ )	$2.5 \times 10^{-6}$	1900	13.7	377	9 HV1800	9 Si <sub>3</sub> N <sub>4</sub> > 99 Mg < 0.15 Cu < 0.2 Al < 0.12 Fe < 0.01
Si <sub>3</sub> N <sub>4</sub> (宇部 興産)	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	0.5-1.5	10-100									N > 98% O 0.49% Fe < 350ppm Ca < 600ppm Al < 150ppm Y 0.39%
チタニウム (チタニウム工業)	K <sub>2</sub> O-6TiO <sub>2</sub>	0.4-1.5	10-100	3.3	0.22		$6.9 \times 10^{-6}$	1350 (融点)	5-7	280	4 (旧E-7)	
ZnO (松下機器)		1-3	20-300	5.78			$4 \times 10^{-6}$	1720 (融点)	9.8	343	27	
9Al <sub>2</sub> O <sub>3</sub> · 2B <sub>2</sub> O <sub>3</sub> (四国化成)		0.5-1.0	10-30	2.93			$4.2 \times 10^{-6}$	1420- 1650 (融点)	8.0	400	7 (旧E-7)	27 Al <sub>2</sub> O <sub>3</sub> 80

Key:

- |                                 |                                    |
|---------------------------------|------------------------------------|
| 1. Whisker                      | 15. Tateho Chemical Industries Co. |
| 2. Phase                        | 16. Ube Industries                 |
| 3. Diameter                     | 17. Ti/acid/K (Titan Kogyo)        |
| 4. Length                       | 18. Matsushita Kiki                |
| 5. Specific gravity             | 19. Shikoku Chemical Corp.         |
| 6. Specific heat                | 20. Trace quantity of free C       |
| 7. Thermal conductivity         | 21. Trace                          |
| 8. Linear expansion coefficient | 22. Oxidation temperature          |
| 9. Heat resistant temperature   | 23. Decomposition temperature      |
| 10. Tensile strength            | 24. New Morse                      |
| 11. Elastic modulus             | 25. Ordinary temperature           |
| 12. Hardness                    | 26. Melting point                  |
| 13. Component                   | 27. Old Morse                      |
| 14. Tokai Carbon Co.            |                                    |

ideal strength to about one-tenth of that. Figure 3 shows an example of measured values of whisker strength. The dispersion in diameter and strength has become one of the factors which make it difficult to predict the strength of whisker reinforced alloys and to disperse strength of composite materials.

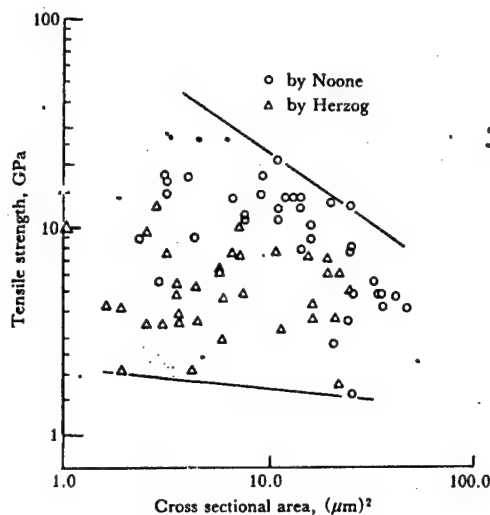


Figure 3. Results of SiC Whisker Tensile Test<sup>(30)</sup>  
(showing the dispersion in diameter and tensile strength)

### 3. Process

As a whisker reinforced alloy matrix, Al alloys have been used in order to obtain materials with light weight and high strength. The production of still lighter Mg alloys and Ti alloys has been meager due to the corrosion resistance with the former and to poor stability of the interface with whiskers with the latter.

Methods for combining whiskers and matrix Al alloys are roughly divided into two --squeeze casting and powder metallurgy.

#### 3.1. Squeeze Casting

This method involves producing a compact of whiskers in advance using compression or screening, setting it in a die to press in a molten Al alloy between whisker gaps, solidifying it while applying a pressure of 500 to 1000 atm and thereby obtaining a whisker reinforced alloy<sup>(1)</sup>. Figure 4 presents the outline of the squeeze casting method using horizontal squeeze caster. This method enables mechanical parts comprising whisker reinforced alloys to be produced with extremely good productivity. However, since a molten Al alloy and whiskers come into contact for 10 sec to 1 min, a reaction occurs between whiskers and matrix, thereby sometimes deteriorating whiskers. Above all, Ti acid K whiskers are generally poor in wettability and susceptible to deterioration by an Al molten metal. The use of a silica-system ceramic binder, when

producing whisker compacts, causes Mg components in an Al alloy to be trapped by the binder, thereby sometimes resulting in Mg segregation in direction of the molten penetration. In order to obtain sound whisker reinforced alloys of good quality, it is necessary to properly control production conditions, such as compact preheating temperature, molten metal temperature, penetrating rate and final squeeze pressure.

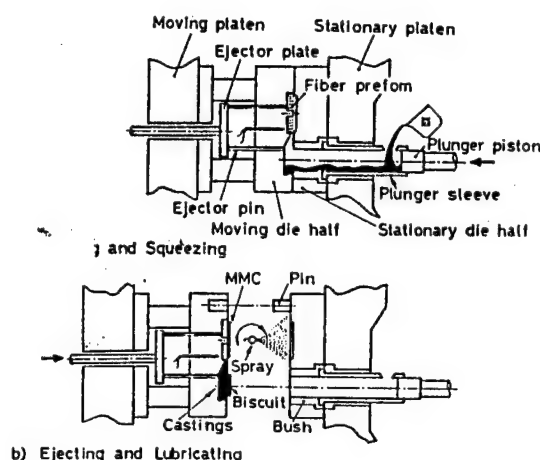


Figure 4. Outline of Manufacturing Processes for Whisker Reinforced Alloys by a Mass Production Horizontal Type Squeeze Casting Machine<sup>(32)</sup> (molten metal temperature, 780°C; die surface temperature, 290°C; plunger rate, 25 mm/sec; squeeze pressure, 49 MPa; cycle time, 80 sec)

### 3.2. Powder Metallurgy

First, a homogeneous mixed body of whiskers and an Al alloy matrix is produced by mixing whiskers and Al alloy powder (normally 10 to 44  $\mu\text{m}$  in grain size) with water or organic solvents such as alcohol into slurry, or by charging whiskers and Al alloy powder into a cyclotron with turbulent air current. This mixed body is compressed and dried to produce a green compact, which is sintered by hot press or HIP to produce a whisker reinforced alloy. Sintering temperature used is 450 to 550°C below the solidus curve. Low process temperature, compared to that for squeeze casting, barely causes deterioration in whiskers resulting from reaction. However, it takes 30 minutes to 4 hours for sintering, which makes this method, in comparison to squeeze casting, inferior in productivity.

The use of either squeeze casting or powder metallurgy generally results in three-dimensional random or discontinuous orientation of whiskers in matrix alloys, thereby enabling forging, rolling and extrusion for secondary processing. Connecting rods are produced by full enclosed die forging, while plates and rods and filaments are produced by rolling and extrusion. Secondary processing including extrusion enables tensile strength to improve by 10 to 20 percent, compared to one before processing<sup>(3, 25)</sup>.

#### 4. Heat Resistance and High Temperature Strength

##### 4.1. High Temperature Retention Property

Whisker reinforced Al alloys, even when heated to above the melting point of the matrix, do not fuse nor become slimy but continue to retain their original shapes; therefore, it is necessary to apply pressure to collapse their shapes. While the oxidation resistance of these materials have not yet been examined, when these materials are retained in air at medium and high temperatures of from 200 to 500°C is considered good as long as no interface reaction occurs, since both whiskers and matrix Al alloys are relatively stable in this temperature area. An examination of the strength deterioration at ordinary temperature after retaining at high temperature has found that, with SiC whisker reinforced 2124 alloy T6 ( $V_f=20\%$ ), its retention at 300°C for 100 hrs causes the strength to decrease by 30 percent and that; with Ti/acid/K whisker reinforced pure Al ( $V_f=20\%$ ), its retention at 500°C for 50 hrs causes the strength to decrease by 30 percent<sup>(5)</sup>. The rate of decrease in strength after retaining medium and high temperatures differs depending on types of whiskers and matrices. With all whisker reinforced alloys, the interface is not stable to some extent, affecting mechanical properties sensitive to texture.

##### 4.2. Ordinary Temperature Strength

With respect to short time strengths, whisker reinforced Al alloys, ordinary temperature tensile strengths and bending strengths are, as shown in Figures 5 and 6, considerably different depending upon types of whiskers, volume percentage of whiskers and matrix alloys. The strength of the whisker reinforced alloy obtained by reinforcing 7075 and 2024 alloys using SiC whiskers and by treating with T6 is the highest with a tensile strength of 610 MPa obtained for a fiber volume percentage ( $V_f$ ) of 30 percent. The second highest is that of the whisker reinforced alloy making use of  $\text{Si}_3\text{N}_4$  whiskers. The disadvantage of Ti acid K whiskers is that they are liable to react with molten Al. Manufacturers have recently developed those with close to  $\text{K}_2\text{O} \cdot 6\text{TiO}_2$  structure, insusceptible to reaction. Also, boric acid alumina whiskers and zinc oxide whiskers with unique shapes shown in Table 1 have been put on the market in recent years. An early(?) initial evaluation of these three whiskers has found that they seem to be less effective for reinforcing Al alloys, compared to SiC and  $\text{Si}_3\text{N}_4$  whiskers (Figures 5 and 6). Compared to SiC and  $\text{Si}_3\text{N}_4$  whiskers, however, they are superior in profitability and can be anticipated for the future, depending upon fields of their applications.

Whether the squeeze casting method or the powder metallurgy method (HIP) were used, the maximum strength at ordinary temperatures won't be so different<sup>(6,35)</sup>, but at high temperatures the powder metallurgy method gives the slightly higher maximum strength (Figure 7). It is worth watching, however, that those by the former method provide whisker reinforced alloys higher in that at high temperature (stated later). On the other hand, the author's experience finds that whisker reinforced alloys which have undergone HIP sintering by the powder method are highest in the strength reliability and, with 20% SiC<sub>w</sub>/6061 T6 extruded materials, an average tensile strength of 545 MPa and a Weibull factor of 48.8 have been attained.

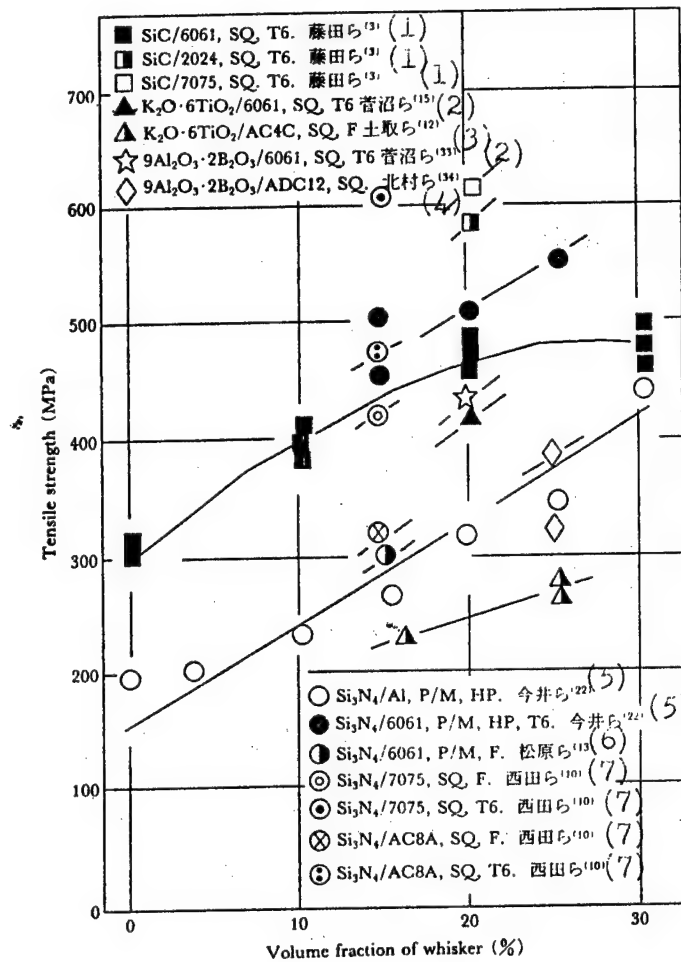


Figure 5. Influence of Types and Volume Percentage of Whiskers on Tensile Strength of Whisker Reinforced Al Alloys

Key:

1. Fujita, et al<sup>(3)</sup>
2. Suganuma, et al<sup>(15)</sup>
3. Tsuchitori, et al<sup>(12)</sup>
4. Kitamura, et al<sup>(34)</sup>
5. Imai, et al<sup>(22)</sup>
6. Matsubara, et al<sup>(13)</sup>
7. Nishida, et al<sup>(10)</sup>



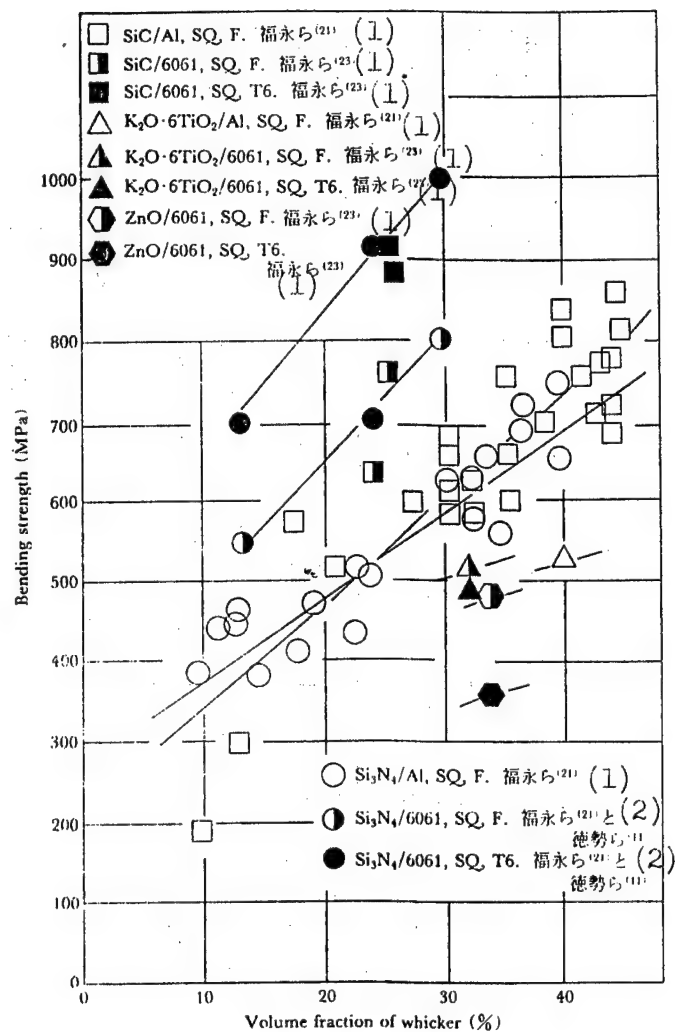


Figure 6. Influence of Types and Volume Percentage of Whiskers on Bending Strength of Whisker Reinforced Alloys

Key:

1. Fukunaga, et al<sup>(21)</sup>
2. Fukunaga, et al. and Tokuse, et al.<sup>(11)</sup>

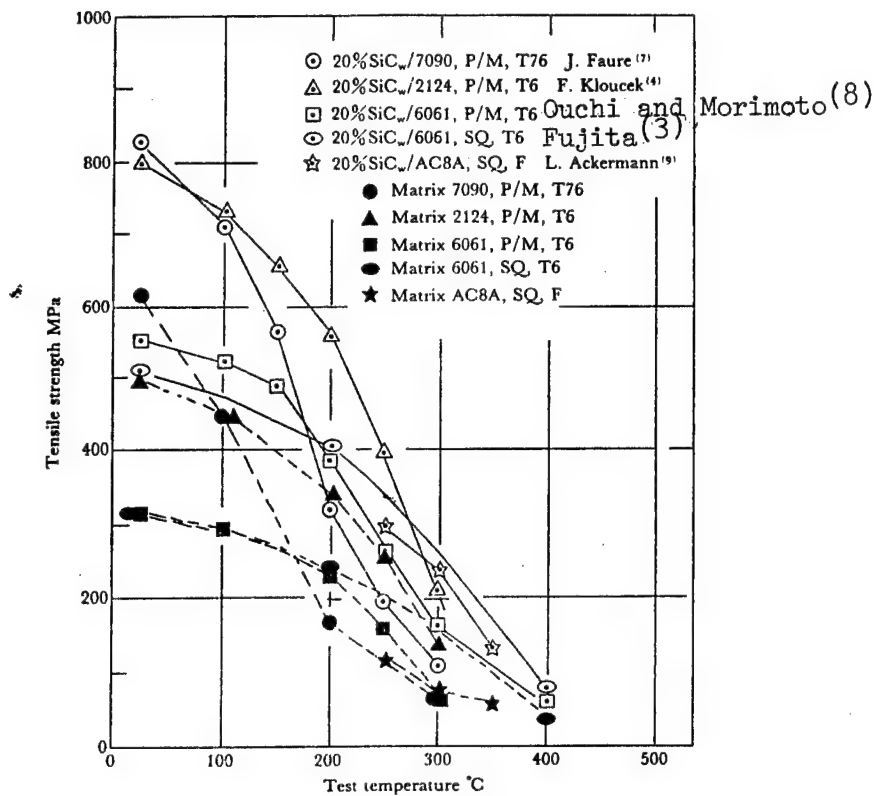


Figure 7. Influence of Types Processes and Test Temperature of Matrix Alloys on High Temperature Tensile Strength of SiC Whisker Reinforced Al Alloys

#### 4.3. High Temperature Strength

Since the high temperature strength is one of the properties most expected with whisker reinforced Al alloys, a large number of research reports have been made on it. Figures 7, 8 and 9 present summaries of high temperature strengths of Al alloys making use of SiC whiskers, Si<sub>3</sub>N<sub>4</sub> whiskers and Ti/acid/K whiskers, respectively.

With SiC whisker reinforced Al alloys (Figure 7), the use of age-hardening type Al alloys, such as 7090 and 2124, for matrix shows high strength at ordinary temperature but a remarkable decrease in tensile strength as the temperature rises during the experiment. In the figure, changes in strength of matrix with test temperatures are shown with the same marks painted black and a comparison of these black marks with their white counterparts finds that the two groups show almost the same trend. This results from the relationship between tensile strength of whisker reinforced alloys and matrix strength can be stated as the following expression. According to the combination law, tensile strength of a whisker reinforced alloy, from the standpoint of decision theory, is:

$$\sigma_c = \beta \sigma_w V_w + \sigma_m (1 - V_w) \quad (1)$$

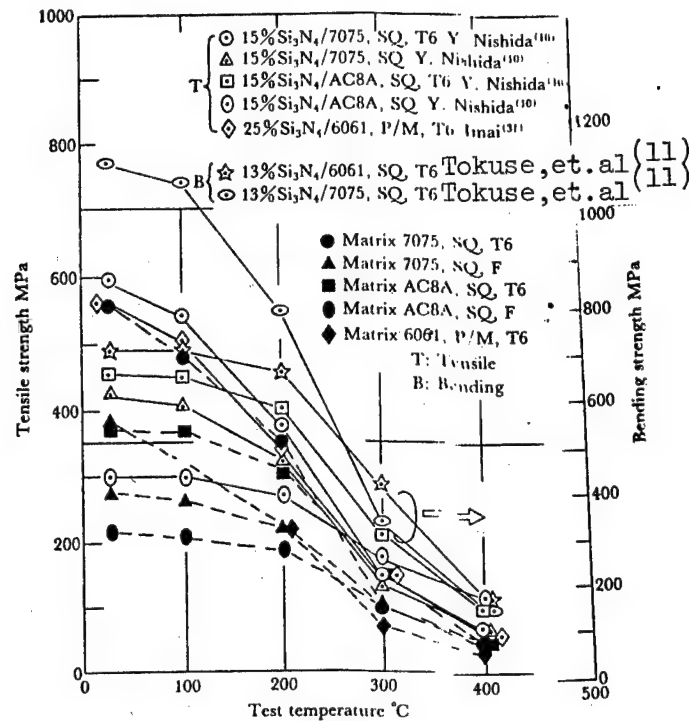


Figure 8. Influence of Types, Processes and Test Temperatures of Matrix Alloys on High Temperature Tensile Strength of  $\text{Si}_3\text{N}_4$  Whisker Reinforced Al Alloys

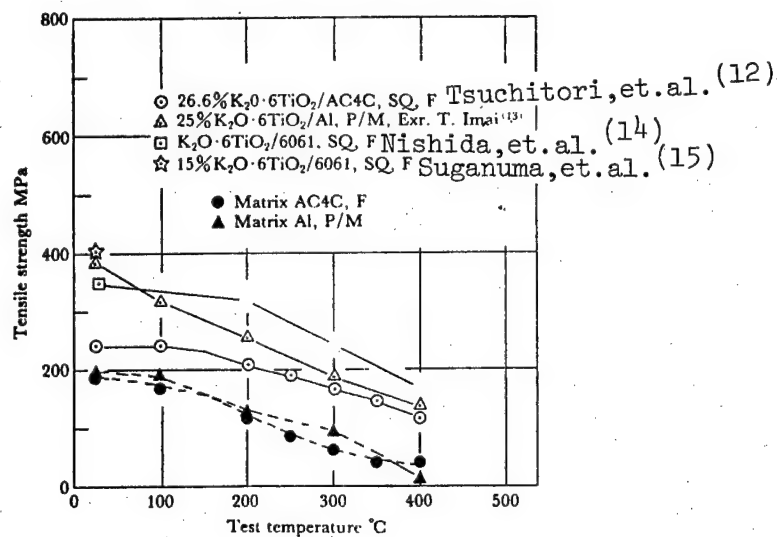


Figure 9. Influence of Types, Processes and Test Temperatures of Matrix Alloys on High Temperature Tensile Strength of  $\text{K}_2\text{O} \cdot 6\text{TiO}_2$  Whisker Reinforced Al Alloys

where  $\sigma_c$ ,  $V_w$ ,  $\sigma_w$ ,  $\sigma_m$  and  $\beta$  represent tensile strength of a whisker/Al composite material, whisker volume percentage, whisker tensile strength, Al tensile strength against whisker fracture distortion and a factor to be determined by whisker orientation configuration, respectively. Adopting 1/5 as a value of  $\beta$ , since whisker orientation is close to three-dimensional random, and substituting 9 GPa, the average value in Table 1, for  $\sigma_w$  makes the first term in expression (1), i.e., a stress in charge of a whisker, and the 2nd term, i.e., a stress in charge of a matrix, almost equivalent. In other words, a matrix contributes greatly to the strength of Al alloys reinforced with discontinuous fibers such as whiskers. A comparison of tensile strengths of whisker reinforced alloys in the temperature area of above 250°C in Figure 7 with materials by the powder method (P/M) and materials by squeeze casting (SQ), finds that those of materials by squeeze casting are higher. This trend remains unchanged with different types of whiskers. In other words, materials by squeeze casting are superior in high temperature strength, and therefore, more stable at high temperature.

The temperature dependency for  $\text{Si}_3\text{N}_4$  whisker reinforced alloys (Figure 8) is quite as strong as that of SiC whisker. Materials produced by squeeze casting are lower in strength at low temperature than those by the powder method, while the strength increases at high temperature above 250°C. This is the same with SiC whisker. The absolute value of tensile strength of Si whisker reinforced alloys seems to be small, compared to SiC whisker.

Ti/acid/K whisker (Figure 9) reinforced alloys feature a bare decrease in strength at high temperature. The strength of matrices considerably decreases with a rise in temperature, so it is impossible to explain high temperature strength of their composite materials using expression (1) in the same manner as with ordinary temperature. Ti/acid/K whiskers are hard to get wet together with molten Al alloys, but once they get wet, they form a very rigid interface, which is found in fracture observation. Also, T6 treatment of  $\text{SiC}_w/\text{Al}$  alloys and  $\text{Si}_3\text{N}_4/\text{Al}$  alloys enables the hardness to increase by 10 to 20 percent, while, with Ti/acid/Al alloys, their T6 treatment causes the hardness to remain or decrease. This conceivably results from some inter-reaction with Al alloy matrices, but it is unknown at this time.

#### 4.4. Thermal Cycle and Creep Property

An experiment involving a tensile test after 500 repetitions of heating and cooling between 100 and 475°C of  $\text{Si}_3\text{N}_4$  whisker reinforced Al and AC8A alloys<sup>(17)</sup> finds that ordinary temperature strength does not decrease at all. Thermal impact was applied to 20%  $\text{SiC}_w/\text{AC8A}$ , T6 material by rapid heating and quenching at between 150 and 400°C and the length of a thermal crack after 4000 cycle was compared with matrix AC8AT6 with a result that the crack was 7 mm long with the composite and 75 mm long with the matrix material<sup>(18)</sup>. Since whiskers are small and matrices are large in coefficient of thermal expansion, a stress accompanying differential thermal expansion naturally occurs locally with each heat cycle; however, it is considered that because of fibers being discontinuous and surrounded by ductile matrices, a stress is moderately relaxed to withstand heat cycle. The result of measuring changes in dimension accompanying heat cycle<sup>(19)</sup> is relatively stable with minor changes in dimension.

Figure 10 presents the effect of SiC whisker reinforcement on steady creep rates<sup>(20)</sup>. According to the figure, loading 20% SiC whiskers into 6061 causes the steady creep rate to decrease remarkably. While self-diffusion activation energy of Al is 140 kJ/mol. creep activation energy of 20% SiC<sub>w</sub>/6061 is as great as 390 kJ/mol. As shown in Figure 10, however, it must be noted that the stress dependency of the steady creep rate is so great that the steady creep rate on the high stress side will be greater than the one of 6061. Figure 11

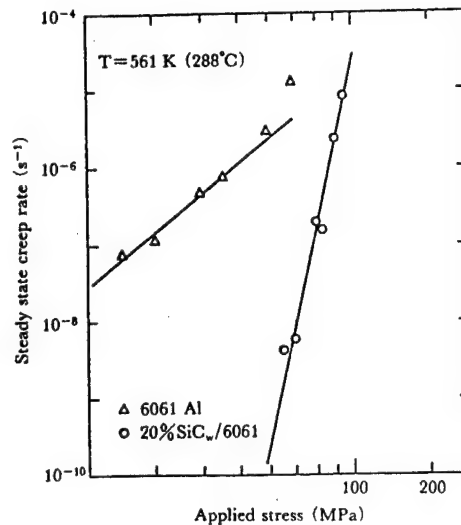


Figure 10. Comparison of Creep Rates Between SiC Whisker Reinforced Alloys and Matrix 6061<sup>(20)</sup>

shows the result of a creep rupture test of a 8-mm bolt made of a 20% SiC<sub>w</sub>/6061 SQ material<sup>(24)</sup>. Compared to matrix 6061, whisker reinforcement has caused rupture life to increase four to five times. As a feature of whisker reinforcement, it is found that the effect of the reinforcement is greater at a higher temperature of 473 K than at 423 K.

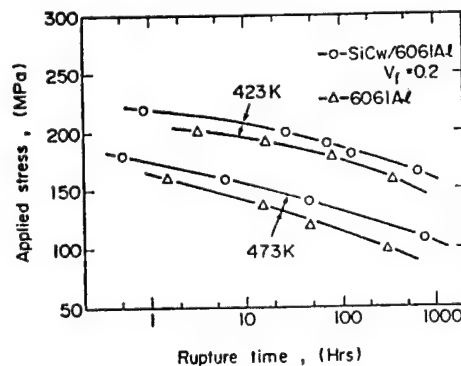


Figure 11. Creep Rupture Strength of Whisker Reinforced 6061 Alloy Bolts<sup>(24)</sup>

It is necessary to know characteristic properties of whisker reinforced alloys other than high temperature strength before they are used in heat resistant environment. They are as follows:

- (1) Specific strength and specific rigidity are equivalent to those of Ti (Table 2);
- (2) Superiority in wear resistance;
- (3) Low coefficient of thermal expansion (Table 3);
- (4) Being well withstandable to radiation, vacuum and electromagnetic environment.

It is known that ordinary temperature characteristics of these properties are surpassing; however, their properties at high temperature have not necessarily been investigated sufficiently, so there will be further research in the future.

Table 2. Comparison of Specific Strength and Specific Rigidity Between SiC Whisker Reinforced Al Alloys and Their Competitive Materials

	20%SiC <sub>w</sub> /6061Al	20%SiC <sub>w</sub> /2024Al	Al-Li	Ti-6Al-4V	6061Al
Tensile strength (MPa)	560	700	530	1100	320
Specific strength (10 <sup>3</sup> m)	20	26	21	25	12
Rigidity (GPa)	110	110	80	114	70
Specific rigidity (10 <sup>6</sup> m)	4.0	4.0	3.1	2.6	2.6
Elongation rate (%)	5.3	5.0	6	16	29
Density (g/cm <sup>3</sup> )	2.8	2.8	2.6	4.4	2.7

Table 3. Thermal Properties of SiC Whisker Reinforced 6061 Alloys

	20%SiC <sub>w</sub> /6061, T6	6061-T6
Thermal expansion coefficient 25~180°C, 1/°C	$14.8 \times 10^{-6}$	$24.0 \times 10^{-6}$
Specific heat J/g·K	0.839	0.896
Thermal conductivity W/m·K	143	167

## 5. Working Temperature Limit and Its Improvement

Compact and lightweight machines and instruments are always demanded and their materialization mainly depends upon the progress in material technology. Materials usable at high temperature and high speed and under special environmental conditions are required and application conditions have currently been complex and severe. Of a great number of conventional materials, whisker reinforced alloys can withstand high temperature with high specific strength and high specific rigidity, which is their first advantage in contributing to

the miniaturization and improved performance of machines and instruments. Available temperatures by the current technical level are probably up to about 350°C, as shown in the temperature dependency of high temperature strength in the previous chapter. The designable applications of this temperature, however, seem to be extremely few since whisker reinforced alloys, as structural materials responsible for strength, are so small in fracture stress that allowable stress becomes several tens of MPa. In moderate applications in which strength is regarded as secondary and light weight, heat resistance, electromagnetic properties and environmental hazard-resistant properties are required, temperatures around 350°C are probably the limit of the availability at the current technical level.

The means of improving the working temperature limit of whisker reinforced alloys are structural materials, according to the combination law of expression (1), in principle, include (1) an increase in whisker volume percentage, (2) improvement in matrix strength, (3) improvement in strength of whiskers themselves and (4) control of the orientation character of whiskers. The following are descriptions of these means.

#### 5.1. Limit of Improved Whisker Volume Percentage

While an increase in whisker volume percentage is related to the improvement of the process of composite materials, about 60 percent is the limit of improved whisker volume percentage  $V_f$ . A further increase in  $V_f$  generally causes whiskers to be broken or damaged, and therefore does not result in an increase in strength as expected. Also, as long as matrices have strong temperature dependency, it is doubtful whether a further increase in  $V_f$  leads to the improvement in high temperature resistance of creeps, etc. Therefore, if ultimate  $V_f$  of 100 percent, i.e., ceramic whiskers, is intended, a proper increase in  $V_f$  will be up to 30 percent.

#### 5.2. Matrices Other Than Al Alloys

Matrices are responsible for about half the strength of whisker reinforced alloys already produced. Therefore, the improvement of matrix strength leads to improved strength and extra super duralumin 7075, super duralumin 2024 and Lo-Ex alloys are utilized. Ordinary temperature strength has been improved by providing aging treatment, but, after all, they are Al alloys and the treatment cannot lead to the improvement of strength in the temperature area over 200°C. In this context, an attempt to use the iron system for matrices<sup>(26)</sup> is being made in order to improve high temperature properties. With  $\text{SiC}_w$ /gray cast iron, Fe-Si intermetallic compounds are generated in the interface and a problem remains unsolved with respect to homogeneous dispersion of fibers.

It is considered that SiC whiskers will serve the lighter weight and the improvement of high temperature properties if the combination of them with Ti alloy matrices is successful. Research into continuous  $\text{SiC}_{\text{CVP}}/\text{Ti-6Al-4A}$  composites has been made and its result obtained; however, because whiskers are so fine in fiber that the deterioration in strength, resulting from the reaction when combined, is remarkable. No examples of success have so far been reported. Thick SiC whiskers have been put on the market in succession

in recent years and it is hoped that Ti alloy matrix composites will be developed. These are produced by applying electroless plating to metal protection films making use of whisker superdispersion paradium colloid<sup>(27)</sup> or by making use of low temperature combination--electric plating, for example. Research on whisker reinforced composites with NiAl intermetallic compounds as matrices has recently been conducted, which have been watched as those aimed for light weight and high temperature properties<sup>(28)</sup>. Making use of the reactivity of Ti/acid/K whiskers with molten Al, the author, et al, produced a stable reactive product to reinforce a matrix as a molten metal penetrates, thereby achieving improved heat resistance and wear resistance. This approach is called reaction control squeeze casting. Based on the same idea, Suganuma, et al<sup>(16)</sup>, oriented Ni powder in inorganic fibers, as shown in Figure 12, during the application of FRMs to pistons, thereby obtaining Ni<sub>3</sub>Al-dispersed composites with superior wear resistance. Such a new attempt is expected, in the future, to generate an intermetallic compound in a matrix and to modify matrix high temperature properties, thereby increasing high temperature strength around 400°C. The use of an intermetallic compound (IMC)

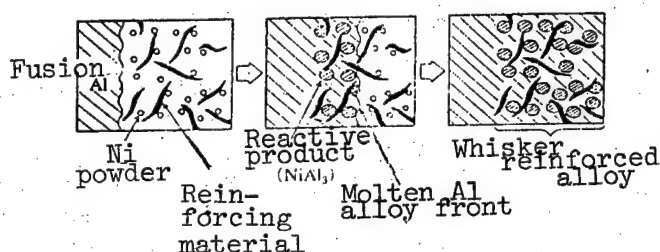


Figure 12. Wear Resistance of SiC Whisker Reinforced AC8A<sup>(3)</sup> (partner material, eutectic cast iron; sliding velocity, 2 m/sec; lubrication, refrigerating machine oil)

for a matrix is expected to provide high strength at above 500°C, regarded as a research subject for the future.

### 5.3. Effects of Whisker Orientation

The whisker reinforcement efficiency would increase five times<sup>(29)</sup>, if all whiskers were a length greater than the critical one, and could be oriented from three-dimensional random to one-way orientation. According to experimental values in Figures 7 and 8, the first term in expression (1), i.e., the share ratio of whisker strength, is between 0.26 and 0.5 at ordinary temperature. Assuming that a squeeze cast material is oriented on a completely three-dimensional random basis, changing this distribution to the one-way orientation will result in a 2.04-fold to 3-fold increase in composite strength. An attempt to change the whisker orientation by extrusion or rolling causes whiskers to fracture, and therefore does not result in improved strength as expected. On the other hand, orderly orientation of whiskers before their combination enables strength to increase considerably. For example, there is an attempt to one-way orientation of whiskers by means of an electrostatic



approach<sup>(2)</sup>. A one-way  $V_f$  25% SiC whisker reinforced Al<sub>2</sub>O<sub>3</sub> alloy was produced by squeeze casting and compared with a three-dimensional random whisker compact produced by the conventional method. It is very interesting to find that, as a result, tensile strength increased by 10 to 15 percent in the temperature range between ordinary temperature and 200°C at which the test was conducted.

#### 5.4. Effects of the Improvement of Whiskers Themselves

It is considered that whiskers supplied for the market are considerably different in strength as well as in length. In the process of fracture of composite materials, the weakest fibers first fracture and cause the stress concentration, promoting fracture of adjacent fibers. When load is further applied, the second weakest fibers fracture and increase the fracture probability of adjacent fibers due to the stress concentration. In this way, local fracture makes progress in succession until at last the remaining fibers fail to withstand load applied and fracture. In this process, the presence of fibers shorter than the critical length will cause drawing, which will become defects to cause the stress concentration in a matrix and its adjacent fibers, thereby promoting early fracture of composite materials.

When the matrix is a ductile metal with a stress relaxing ability, fracture strength of a composite material is not necessarily determined by the weakest fibers. The whisker average strength obtained from expression (1) on the basis of measured values of tensile strengths of whisker reinforced Al alloys are 6.3 to 8.3 GPa ( $\beta$  of 1/5 is substituted) at ordinary temperature in Figure 7. Therefore, tensile strength of whisker reinforced alloys will be increased from 1.3 to 1.6 times with three-dimensionally oriented materials and from 3.9 to 5.4 times with one-way oriented materials. Whisker strength may be approached to 13.7 GPa, their maximum fracture strength, by improving the whisker generating method or by selecting whiskers obtained, thus remarkably improving the reliability in strength.

#### 6. Applications of Whisker Reinforced Alloys

Table 4 shows major examples of inorganic fiber reinforced metals developed as commercial products in Japan. It should be acknowledged that these metals, although all of them are not whisker reinforced alloys, show that for them to be adopted against conventional counterparts, they need to possess more than two features as a composite material. In other words, for a whisker reinforced alloy to be put to practical use, it is necessary to possess multiple features so that the whisker reinforced alloy is superior in heat resistance, environmental neutron hazard resistance, low thermal expansion in addition to light weight and high specific strength. At present they are all applied to functional parts and their application to strength parts, such as connecting rods, is anticipated to be in the phase close to commercialization. The second point of the application of whisker reinforced alloys is to regard them, not as materials, but as composite parts for the optimum design with shapes, dimensions and properties taken into account from the beginning of design. In other words, an idea of replacing the material of existing parts with whisker reinforced alloys cannot be accepted. Design engineers as well as molding engineers need to consider adopting shapes, dimensions, fiber orientation and

Table 4. FRA Application Examples in Japan (Commercialized products)

Part Name	FRA System	Process	Features of FRAs Utilized	Remarks
Pressure shroud and vane of hydraulic vane pump	Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> /AC4C	Squeeze casting	Wear resistance, noise damping capacity	Hiroshima Aluminum Industries, Co. (1978)
Piston ring groove of diesel engine	NiO <sub>3</sub> /Al alloy	Squeeze casting	Light weight, medium/high temperature wear resistance	Toyota Jiko [phonetic] (1983)
Golf goods, driver face	SiCpccs/Al alloy	Squeeze casting	Light weight, scratch resistance, fashionability	Nippon Carbon Co. (1984)
Connecting rod of Gasoline engine	SUS thin lined Al alloy	Squeeze casting	Specific strength	Honda Motor Co. (1985)
M8 bolt	SiCw/6061	Squeeze casting, extrusion, rolling	Neutron absorption sectional area, high temperature strength, high vacuum-resistant degasification quality	Toshiba Electric Corporation (1986)
Pipe joint of space structure	SiCw/6061	Squeeze casting, rolling	Specific strength, low thermal expansion, atomic oxygen deterioration resistance	Mitsubishi Electric Corporation (1988)
Rotary compressor vane	SiCw/Al-17% Si, 4% Cu alloys	Squeeze casting	Light weight, wear resistance, low temperature expansion	Sanyou Electric Co. (1989)

volume percentage and partial percentage which enable maximum performance to be generated in the given service conditions. For example, the likelihood of lightening the connecting rod of a high speed internal combustion engine using a whisker reinforced alloy is likely to be effective for thinning the crank shaft, and the crank case, and minimizing the bearing. This necessarily requires redesigning the engine. It is necessary to evaluate total cost performance based on such redesigning.

## 7. Conclusion

The history of whisker reinforced alloys is recent and their use experiences are few and unsubstantiated. Their superior properties, adjustable by the combining process, enable them to be applied to proper spots of machines and instruments with many effects. Such proper spots are found, not by those related to manufacturing or combining whiskers, but by those who design machines and instruments and those who use them every day. The author would like to enlighten these people on the advantages and disadvantages of whisker reinforced alloys and expect their applications at jobsites.

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## Thermal Barrier Coating

906C7532C Tokyo KYOKUGEN KANKYO YO TAINETSU FUKUGO ZAIRYO in Japanese  
20 Jan 90 pp 37-43

[Article by Hiromitsu Takeda, Metallic and Ceramic Materials Research Institute, Toshiba Corporation: "TBC; TBC Key Technologies; Examples of TBC Effects"]

### [Text] 1. Introduction

A gas turbine is a typical system placed in the ultimate state of a high temperature area in practical fields. In recent systems, gas temperature reaches 1300°C and load applied to the turbine blade revolving at peripheral speed exceeding 450 m/sec in that atmosphere is extremely great. No current materials can be used under such environment and the attempt will employ the help of cooling technology. Thermal barrier coating (TBC) described in this article is laminated type composite materials comprising a ceramic layer and a metallic bond layer designed to be usable under environmental conditions with large temperature gradient to back up this cooling technology<sup>(1)</sup>.

### 2. On TBC

TBC is not material technology dedicated for gas turbines, but a gas turbine is selected for explanation as a system in which a remarkable effect can be obtained. A gas turbine involves guiding air and a fuel compressed by a compressor into a combustor, generating a gas flow with high temperature, high pressure and high rate by means of combustion, and obtaining energy by rotating the turbine blade with this gas flow. Since the efficiency of a gas turbine improves as its working temperature rises, devices are made so as to increase combustion temperature as much as possible, one of which is cooling technology for protecting members. In the internal structure of a state-of-the-art gas turbine, complex space is formed and a cooling medium (normally air) flowing in the interior prevents the metallic base from fusing and fracturing due to a high temperature gas flowing outside. The existence of current gas turbines is enabled by contradictory operations of increasing temperature of systems and cooling their members. A further pursuit of system efficiency will need a more careful study of this cooling method and minimizing a quantity of energy lost by cooling.

TBC is material technology which indirectly supports this cooling technology. The following is a description of its principle using an example of the gas turbine cooling blade in Figure 1. In the figure, the right is a conventional cooling blade. Cooling air flowing in the interior of the blade enables the average temperature of the metallic base to be controlled at a considerably lower level than the high temperature combustion gas flowing outside. In this case, however, the quantity of heat flowing from the metallic base to cooling air is not insignificant. On the other hand, in the TBC-applied blade on the left in the figure, a quantity of heat flowing in from the exterior is controlled due to the adiabatic effect of TBC and the large thermal gradient is formed in the TBC layer, thereby enabling the average

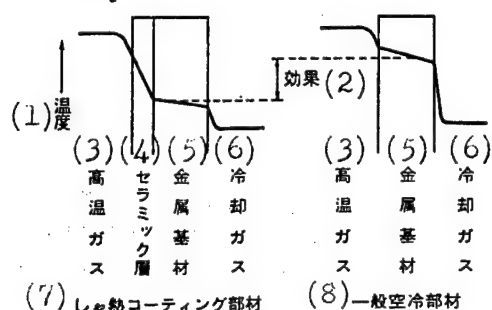


Figure 1. TBC Effect

Key:

- |                         |                                  |
|-------------------------|----------------------------------|
| 1. Temperature          | 5. Metallic base                 |
| 2. Effect               | 6. Cooling gas                   |
| 3. High temperature gas | 7. Thermal shield coating member |
| 4. Ceramic layer        | 8. General air-cooled member     |

temperature of the metallic base to decrease substantially.  $R$ , resistance against the heat flowing into cooling air after passing the TBC layer and the metallic base, can be expressed as

$$R = \frac{1}{\alpha_g} + \frac{L_{ce}}{\lambda_{ce}} + \frac{L_b}{\lambda_b} + \frac{L_m}{\lambda_m} + \frac{1}{\alpha_c} \quad (1)$$

where  $L$ : thickness,  $\alpha$ : heat transfer coefficient,  $\lambda$ : coefficient of thermal conductivity,  $g$ : high temperature gas,  $c$ : cooling gas,  $ce$ ,  $b$  and  $m$  represent thickness, thermal conductivity, high temperature gas, cooling gas, ceramic layer, metallic bond layer and metallic base, respectively. This expression implies that in a field with great thermal conductivity, such as the blade surface of a gas turbine, the presence of a substance with low thermal conductivity in the way of heat passage has influence as great heat resistance even if it has meager thickness. In other words, the feature of TBC is that merely forming a thin layer results in high cooling effect. Figure 2 presents an example of calculation of the effect, which shows that the formation of a TBC layer about 0.3 mm thick enables the average temperature of the metallic base to be controlled at a temperature 100°C lower than one in general cases.

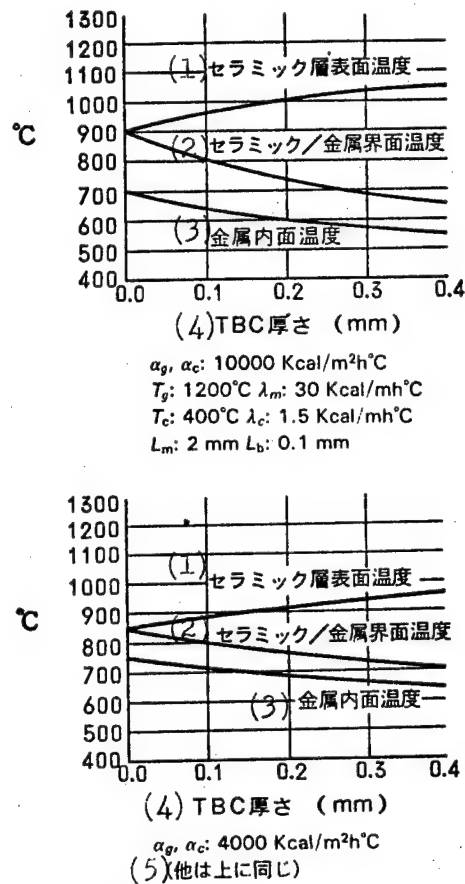


Figure 2. Calculation Examples of TBC Effects  
 (The definition of each symbol is the same with expression (1))

Key:

1. Ceramic layer surface temperature
2. Ceramic/metal interface temperature
3. Metallic internal temperature
4. TBC thickness
5. Others are the same as above

With such a superior property, TBC is expected to find its application in high temperature ultimate environmental equipment, but barriers to its application will not be easy to overcome. As can be found in Figure 2, for example, the temperature difference caused in the ceramic layer comprising TBC exceeds  $200^\circ\text{C}$  in a slight thickness of 0.3 mm, thereby creating problems of a thermal stress due to the thermal gradient in the layer, and a thermal stress due to the difference in thermal expansion coefficient between ceramics and a metal resulting from the ceramic layer being bonded with the metallic base. For the solution to these problems, it will be necessary to refine many technical factors, such as the selection of materials, control of the coating layer, coating methods and surface modification.

### 3. Key Technologies for TBC

#### 3.1. Materials

##### 3.1.1. Ceramic Layer

Properties required for the ceramic layer are as follows:

- ① Low thermal conductivity: This is a primary requirement for the ceramic layer to serve as a resistance against the influx of heat. As shown in the graph of the thermal conductivity and TBC effects of the TBC layer in Figure 3, the thermal conductivity has great influence.

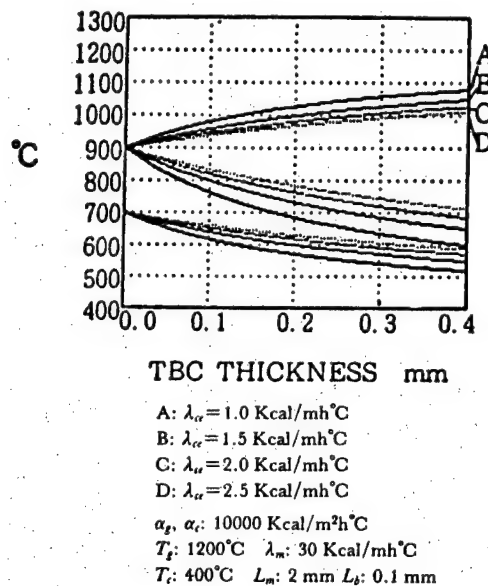


Figure 3. Influence of Thermal Conductivity of the Ceramic Layer on TBC

- ② High temperature stability: Being exposed to a high temperature gas, this layer needs to be insusceptible to high temperature and the reaction to corrosive components in the gas to prevent thermal deterioration.
- ③ High thermal expansion coefficient: Installed on the metallic base, this layer needs to possess, as a requirement, a thermal expansion coefficient close to one of a metal, one high for ceramics.
- ④ High coating formation quality: The basic application form of TBC is forming it into a structural member. Therefore, this layer needs to be applied to proper means of molding in an industrial scale.

The prerequisite that the main layer of TBC be ceramic results from the conditions of guideline numbers ① and ②. Plotting with material properties in



guideline numbers ① and ③ for selecting a ceramic layer results in a property map shown in Figure 4.  $ZrO_2$  is selected by adding the condition of guideline number ④ to this map (as stated later, TBC is formed by plasma thermal spray).

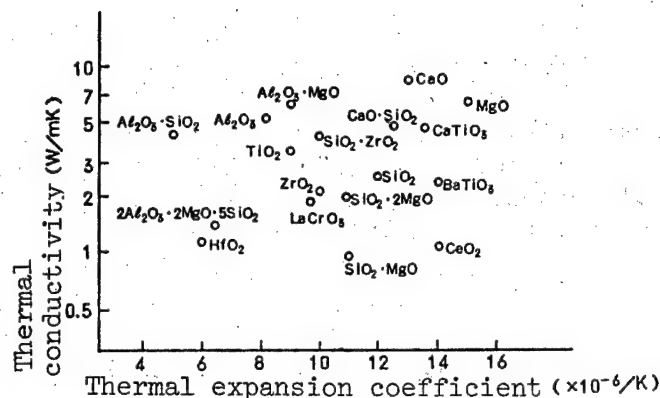


Figure 4. Ceramics Property Map

$ZrO_2$ , as simplex composition, is not suitable for TBC because simplex  $ZrO_2$  undergoes a phase change accompanied by a volume change, according to the change in temperature, and becomes susceptible to damage. In order to control a phase change, other oxides need to be added for stabilization. Oxides used for the stabilization of  $ZrO_2$  include several types, while it is necessary to optimize stabilization materials for TBC used in the near hazardous condition. Figure 5 presents properties as TBC of  $ZrO_2$  using CaO, MgO and  $Y_2O_3$  generally in use for the stabilization materials for  $ZrO_2$ , indicating that the one using  $Y_2O_3$  shows the best property. Also, the addition of  $Y_2O_3$  is an important

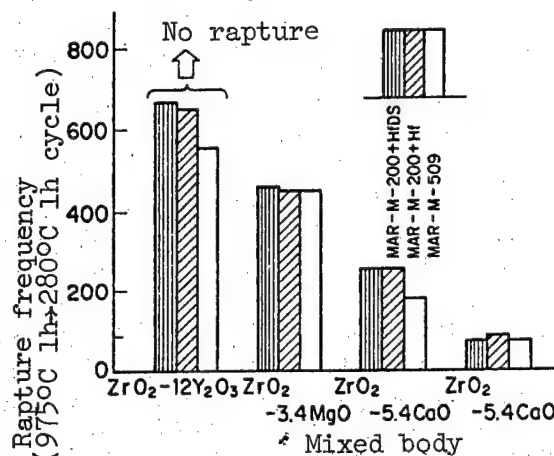


Figure 5. Influence of Stabilization Materials on  $ZrO_2$  Thermal Fatigue Strength

factor and, as shown in the relationship between the addition of  $Y_2O_3$  and properties in Figure 6(3), the addition of 6 and 8 percent of  $Y_2O_3$  shows superior results.

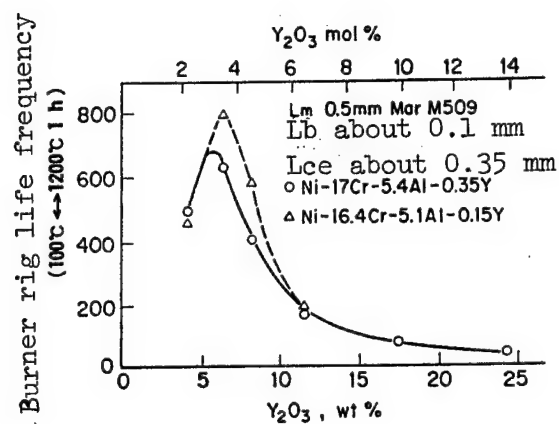


Figure 6. Influence of Y<sub>2</sub>O<sub>3</sub> Addition on ZrO<sub>2</sub> Thermal Fatigue Strength

### 3.1.2. Metallic Bond Layer

The role played by the metallic bond layer is to make a ceramic layer positively bond with the metallic base and to protect this base from oxidation and corrosion. Therefore, material properties required for this layer are superior oxidation resistance and high temperature corrosion resistance<sup>(4)</sup>. Figure 7 presents thermal fatigue properties of this layer as TBC when IN-738 is used for the base and 8%Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> for the ceramic layer. It is found that, compared to Ni-5Al, the most classic material, the use of NiCoCrAlY, developed recently, has enabled life to expand by three digits.

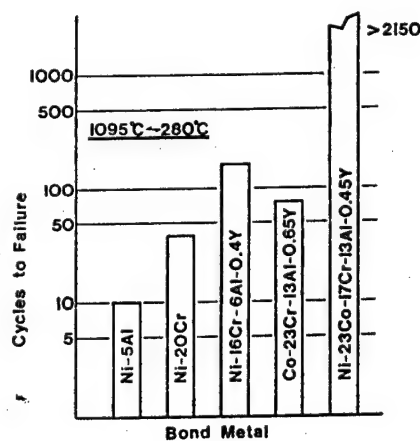


Figure 7. Influence of the Metallic Bond Layer on TBC Thermal Fatigue Strength

### 3.2. Coating Layer formation Technology

Plasma thermal spray is a general method for forming TBC on a metallic base. Research on the formation of a ceramic layer by chemical vapor deposition (CVD) is being made, but the method has not yet been put to practical use.

Plasma thermal spray is a method involving discharging while flowing a gas between the hollow electrodes (See Figure 8), changing the gas into a plasma, charging a coating material into a generated gas flow with high temperature and high speed and instantaneously fusing it for coating. This method enables ceramics with a high melting point to fuse with ease. Furthermore, the method enables coating to be formed at extremely high speed, thereby serving as important means of ceramic coating. Plasma thermal spray is suitable for TBC not only because it is effective as a means of ceramic coating but because it can control coating property. In other words, with respect to the above-mentioned properties required for a TBC ceramic layer, the properties of guideline numbers ① and ③ are affected not only by intrinsic material properties but by the quantity of holes in coating, so their control is important.

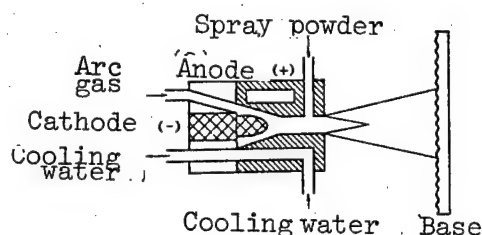


Figure 8. Example of the Internal Structure of a Plasma Spraying Gun

Figure 9 (not reproduced) shows a microtexture of a TBC layer, in which holes can be observed in the ceramic layer. From the standpoint of thermal insulation, the larger the quantity of holes, the better, but this causes the mechanical properties of a TBC layer as a material to decrease too much to be used in a severe gas turbine environment.

Plasma thermal spray, a high speed coating formation method, can be mass produced if it can be put on the industrial production process. However, the application to three-dimensionally complex shape like a gas turbine blade is regarded as very difficult technology since, in order to obtain uniform and homogeneous coating, the following basic conditions are required: ① the distance between the spraying gun and the base to be sprayed is always constant; ② plasma jet is perpendicular to the surface of the base to be sprayed; ③ relative transfer speed between plasma jet and the base to be sprayed is always constant. To accomplish the application, a high level of robot technology is needed<sup>(5)</sup>. Figure 10 presents a general view of a TBC application unit for gas turbine blades developed in the national Moonlight Project. A drive method planned on the basis of the blade section shown in Figure 11 and a thermal spray application program considering the coating formation

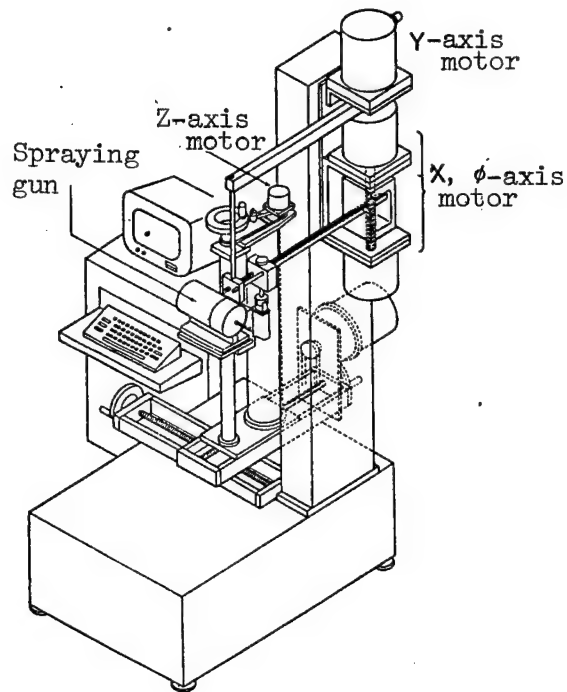


Figure 10. Automatic Plasma Spraying Unit for Gas Turbine Blades

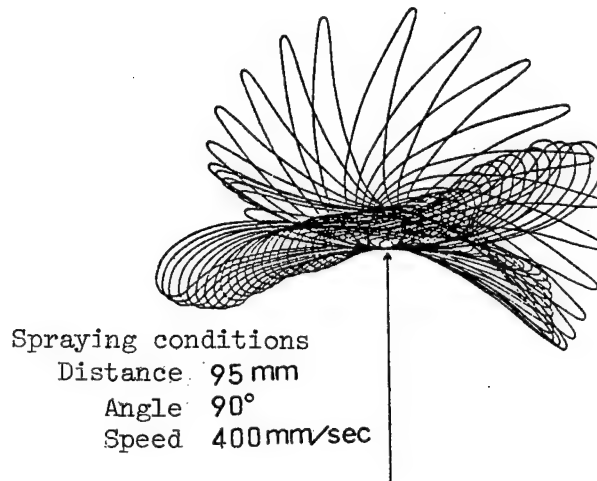
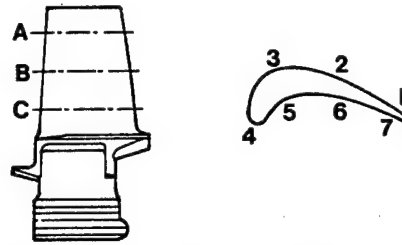


Figure 11. Relative Movement of a Blade with the Spraying Gun when Applying TBC to It

efficiency, specific to plasma thermal spray have enabled homogeneous TBC application, shown in Figure 12, to be conducted.

Table 1. Example of Measuring TBC Thickness  
Using an Eddy Current



		(1) 翼周囲上の位置 (図中の数字に対応)						
		1	2	3	4	5	6	7
(2) 翼長方向の位置	A	135	130	270	370	280	170	170
		185	160	220	100	290	225	190
		1.37	1.23	0.81	0.27	1.04	1.32	1.12
	B	140	120	250	370	260	170	110
		175	155	195	70	310	170	155
		1.25	1.29	0.78	0.19	1.17	1.00	1.41
	C	140	100	200	300	260	180	110
		170	155	200	75	275	195	170
		1.21	1.55	1.00	0.25	1.06	1.08	1.55

(3) マス中 4 上段: Dermatron による測定値  
5 中段: 顕微鏡による測定値  
6 下段: 補正倍率

Key:

1. Position on blade circumference  
(corresponding to numerals in the drawing)
2. Position in the blade length direction
3. In blocks
4. Upper row.....Measured values with Dermatron
5. Middle row.....Measured values with a microscope
6. Lower row.....Correcting magnification

### 3.3. Coating Thickness Measuring Technology

The progress in TBC application technology has basically enabled homogeneous coating formation. In plasma thermal spray, however, since the powder feeding system is driven by a gas, and plasma jet is specified by an arc current and an arc gas, a high-level control of the quantity of molten powder in plasma jet is difficult and it is almost unavoidable for coating to be heterogeneous to some extent. In this context, it is hoped that the thickness of coating can be measured on a nondestructive basis during TBC application or with each product.

Approaches using a supersonic wave, a laser and an eddy are being attempted; however, the porosity and large surface roughness prevent them from becoming effective means. The method using an eddy current will be considerably effective if calibration curves for different measuring conditions are found in advance (See Table 1).

Control of coating thickness is not only required during production, but is desired to be conducted even after it is incorporated into the system. TBC is effective thanks to coating only 0.3 mm thick, as shown in Figure 2, the wear in the surface of a TBC layer for some reason results in a remarkable decrease in effect. A thickness detection probe cannot be inserted into the system in cases which call for some measures. As a method, detection technology, making use of ultraviolet excitation emission, is being attempted. The technology involves comprising a ceramic layer with another layer by a trace quantity of a substance which emits fluorescence when irradiated by an ultraviolet ray, and an ordinary layer, and detecting the state of the surface layer based on the emission caused by the ultraviolet irradiation. The most basic construction comprises layers with thickness of which TBC effect can be expected and those with margin thickness, each having different emission performance. Light emitted when an ultraviolet ray is irradiated includes many types (See Table 2) and a change in color for each unit thickness enables the current state to be known in detail.

Table 2. Types of Add-In Oxides and Fluorescence Emission Colors

Add-In Oxide	Emission Color
$\text{Bi}_2\text{O}_3$	Blue
$\text{TiO}_2$	Bluish white
$\text{Tb}_4\text{O}_7$	Green
$\text{Eu}_2\text{O}_3$	Vermilion
$\text{Sm}_2\text{O}_3$	Orange
$\text{Y}_2\text{O}_3$	Reddish purple

#### 3.4. Surface Modification Technology

What must always be taken into account when actually making use of TBC is the durability and the factors affecting the durability, which include the above-mentioned thermal stress and erosion of the ceramic layer. The ceramic layer has holes in it in order to improve thermal stress resistance and low thermal conductivity. However, the state of porosity is not preferable in terms of erosion properties. As a method for satisfying two conflicting properties, the development of surface modification is being promoted to make close only the surface layer which creates a problem of erosion. The development is related to an approach involving fusing the ceramic surface exclusively, using a laser and thereby making it close<sup>(6)</sup>. Figure 13 (not reproduced) is an example of the experiment, showing that the surface of the porous ceramic layer has become close. The improvement in the erosion properties by this treatment is so remarkable that, compared to the ceramic layer as formed by plasma thermal spray, as shown in Figure 14, erosion loss by the same conditions is reduced to close to one-third, thereby enabling the performance close to that of sintered materials.

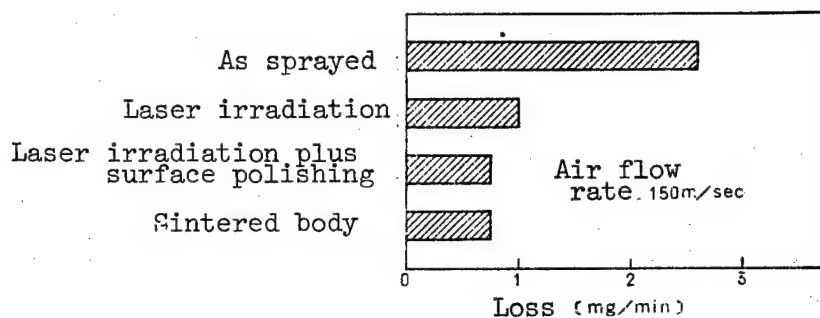


Figure 14. Effect of Laser Surface Treatment on TBC Erosion Loss

#### 4. Examples of TBC Effects

Figure 15 presents an example of the experiment applying TBC to the stationary blade--a blade to control the direction of a gas flow, fixed on the casing--of a gas turbine used in aircraft. The temperature of cooling air flowing in the interior of the blade is considerably low, compared to actual cases, because of which effect it is stressed, showing a good result. This figure implies that a blade without TBC, compared to one with TBC, requires a more than 3-fold quantity of cooling air. The efficiency of a gas turbine largely depends upon how to control the quantity of cooling air, which is why the effect of TBC is significant.

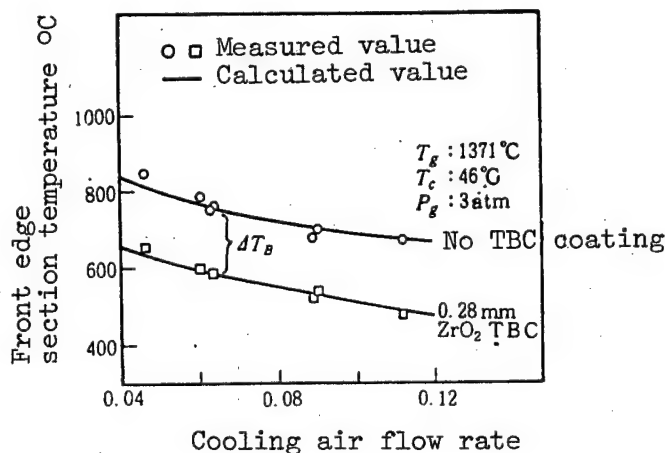


Figure 15. TBC Effects: Model Test Example 1

Figure 16<sup>(17)</sup> presents results of an engine durability test conducted after applying TBC to 14 of 66 stationary blades of domestic aircraft-use gas turbines. The test was conducted under extremely severe conditions, which made it necessary to replace blades, while TBC-applied blades did not need to be replaced in most parts of the entire test process.

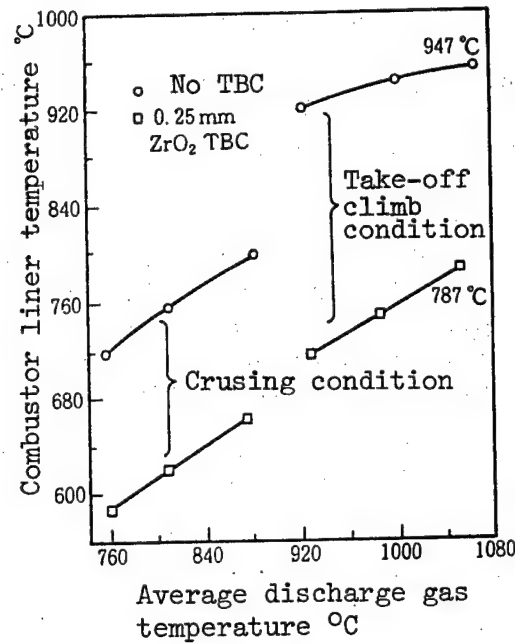


Figure 16. TBC Effects: Model Test Example 2

Figure 17 shows an example of TBC application to the combustor of an aircraft-use gas turbine. The figure shows a remarkable effect during take-off climb when the engine output becomes maximum. This is proof that TBC provides a greater effect in a field of high thermal conductivity.

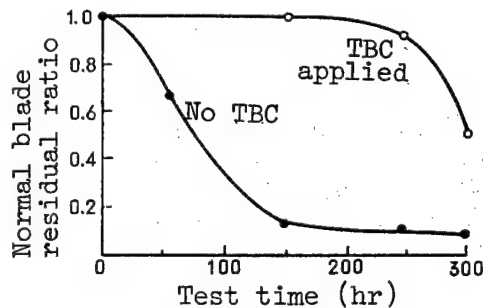


Figure 17. TBC Effects: Model Test Example 3

## 5. Conclusion

TBC is material technology capable of providing a great effect using its thickness of only 0.3 mm or so, but, at present, it is mainly employed on an auxiliary basis in order to prolong system life. The greatest reason for this is that technology involving durability of ceramic coating has not yet been established. Under such circumstances, it is expected that progress will be made in the development of more sophisticated material technology.



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## Functionally Gradient Materials

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[Article by Kazumichi Shiota, Functional Properties Research Division,  
National Research Institute for Metals: "Design of Functionally Gradient  
Materials and Their Production Technology; Applications of Functionally  
Gradient Materials to Other Sectors"]

[Text] 1. Introduction

### 1.1. Need for Functionally Gradient Materials

The earth, once regarded as incredibly large, is currently becoming smaller and smaller in terms of time and space. The reason behind this is progress in the transportation industry, such as space, aviation and automobiles. It is difficult for us to live without these technologies. On the other hand, the quantity of energy consumed in these sectors is becoming excessive as machines become larger in size. When machines become larger in size the energy consumption per head decrease. However, energy consumption, as a whole, increases; thus, we are rapidly and positively consuming earth resources with limited quantity which can never be reproduced.

Various heavy industries are those industries indispensable to our daily lives. The more we desire to lead a rich life, the more active heavy industries, such as steel or power, naturally become and the more energy consumed.

In the future it will become increasingly necessary to develop technologies for the effective use of a limited amount of energy, if we wish to maintain our current lifestyle. In terms of energy, thermal efficiency in use needs to be improved, which, in turn, needs to increase temperature of a high heat source, according to thermodynamics. Temperature of the high heat source side of current equipment is restricted by the heat resisting temperature of materials. Therefore, the development of heat resisting materials is indispensable for solving this problem. This alone is, not a solution to the problem, one of the main factors for the elimination of it.

It is conceivable that nuclear power generation will be one of the prospective candidates in solving energy problems in the near future. The central part of

this technology is the development of ultrahigh heat resisting materials as well as plasma confinement technology. Now the focus is narrowed down to a problem of heat resistance. A space shuttle, for example, needs a speed over Mach 10 and the external surface temperature of the airframe projected to reach 2000 K due to aerodynamic heating. Also, the internal wall of the nuclear fusion reactor is exposed to a 6000-K gas. When considering temperature in a blast furnace to be about 2000 K and that of the solar surface about 6300 K, it is only imaginable how intensely hot the temperature is.

## 1.2. Basic Concept of Functionally Gradient Materials

The main properties required for structural materials include high elastic modulus, high strength and high fracture toughness, which are added by an important factor of light weight with those for use in aviation and space equipment. Metallic materials are superior in all of these properties, and best suited for structural materials. For example, the elastic modulus of typical Fe is 205 GPa and one called high strength steel has about 800 MPa and toughness value  $K_{IC}$  as large as about 50 MPa  $\sqrt{m}$ , being strong against mechanical impact. Structural materials for use in aviation and space equipment need lightness in weight as well as high strength and high elastic modulus. These properties are represented by strength and elastic modulus per density, i.e., specific strength and specific elastic modulus. With density of 7.8 g/cm<sup>3</sup>, specific strength and specific elastic modulus of Fe are  $1.03 \times 10^6$  cm and  $2.6 \times 10^8$  cm, respectively. With a high elastic modulus of 400 GPa and a density of 19.3 g/cm<sup>3</sup>, W is smaller in elastic modulus than Fe. However, if importance is attached to strength and low elastic modulus is allowed, a density of 4.5 g/cm<sup>3</sup> and strength equivalent to that of Fe with Ti, while, with Al alloys, a density of 2.7 g/cm<sup>3</sup>, about one-third that of Fe, strength half that of Fe can be obtained.

On the other hand, with respect to heat resistance in the abovementioned air, W(3653 K), Ta(3250 K) and Mo(2890 K) which are called refractory metals are high in melting point, but extremely low in oxidation resistance at high temperature. Therefore, Ni and Co alloys are used for jet plane turbines, etc. Their heat resistant temperature is about 1320 K at the moment.

With respect to heat resistance, ceramics are overwhelmingly dominant. Ceramics, defined differently depending upon purposes of their application, can be said to be an inorganic material as opposed to other metals produced through high temperature. The majority of ceramics are such metals as Al, Ti, Zr and Cr or oxides, carbides, nitrides, borides and silicides of metalloids such as Si, sometimes including simple substance elements, such as B, C and Si.

Among these materials, many can be found with a melting point and a sublimation point of, aside from 6000 K, above 2000 K. Of simple elements, the sublimation point of C is the highest, 3700 K. C is liable to improve its strength until temperature reaches about 2500 K rather than at ordinary temperature, while it undergoes remarkable oxidation in air at above 700 K, making it difficult to be used as is. The melting point of alumina, the most popular of ceramics, is 2323 K, while that of zirconia, well known as fine ceramics is 2950 K; both having high heat resistance. Some, as is the case with TaC, have

a melting point of 4153 K. It is not a rare thing to find ceramics with an elastic modulus of above 200 GPa, while, with fabric ones, a strength of about 3 to 4 GPa can be obtained. However, their fracture toughness value  $K_{IC}$ , another important factor as a structural material, is as small as 5 to 9 MPa  $\sqrt{m}$ , which shows that they are weak against mechanical impact.

While heat resistant ceramics have a thermal expansion coefficient ( $\alpha$ ) of  $5 \times 10^{-6} \text{deg}^{-1}$  and a thermal conductivity ( $K$ ) of  $0.1 \times 10^{-2} \text{W.m}^{-1}\text{deg}^{-1}$ , small values, those of ultrahigh heat resistant alloys are as large as  $12 \times 10^{-6} \text{deg}^{-1}$  and  $0.9 \times 10^{-2} \text{W.m}^{-1}\text{deg}^{-1}$ , thereby showing their difference in thermal properties.

As stated above, since the surface is in contact with a high temperature gas exposed to very high temperature, it needs heat resistance. In order to prevent the heat from being transmitted to the interior, thermal shielding quality is necessary. As apparent from the above properties, ceramics materials are suitable for such portions.

On the other hand, a space shuttle has, as a fuel, liquid hydrogen (14 K) in the interior to be used for cooling its sections as well. With nuclear reactors, a liquid metal (400 K) is used for cooling use. Cooling for these machines and equipment naturally needs a large flow of heat and structural materials to support them, which require sufficient strength. Metals with high toughness and high thermal conductivity are superior.

With these conventional materials, even when they are not of a single material but a mixed body of more than one type of material, such as particle dispersed alloys, efforts have been made to mix them homogeneously as shown in Figure 1 (a). With these materials, all properties, such as heat resistance, thermal expansion coefficient, etc., led by dynamic property, are homogeneous in the interior of materials as shown on top of the figure.

In space shuttles and nuclear reactors, conflicting demands need to be met with an integral material due to the spatial restriction, etc. in many cases. To cope with such severe environmental conditions, much research has been energetically carried out to date on heat resistant ceramics materials, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiC}$  and  $\text{Si}_3\text{N}_4$ , or Ni- and Co-radical ultrahigh heat resistant alloy materials. However, it is nearly impossible for a single material to meet the demand for considering both heat resistance and mechanical properties.

To cope with this, such attempts were made for integral materials, suitable for high and low temperatures, to individually share functions. In the case of a space shuttle, for example, where a ceramics material superior in heat resistance and thermal shielding quality is applied to the surface of the air-frame made of a metal with high toughness, or to provide an ultrahigh heat resistant alloy with thermal shielding quality by means of surface coating of heat resistant ceramics, with respect to turbine blades. With these materials, as shown in Figure 1 (b), a different phase interface necessarily exists in their interior and, as shown in the top of the figure, the different phase interface is greatly different in physical and chemical properties. Therefore, when a conjugate with ceramics applied on the metal surface is heated, for

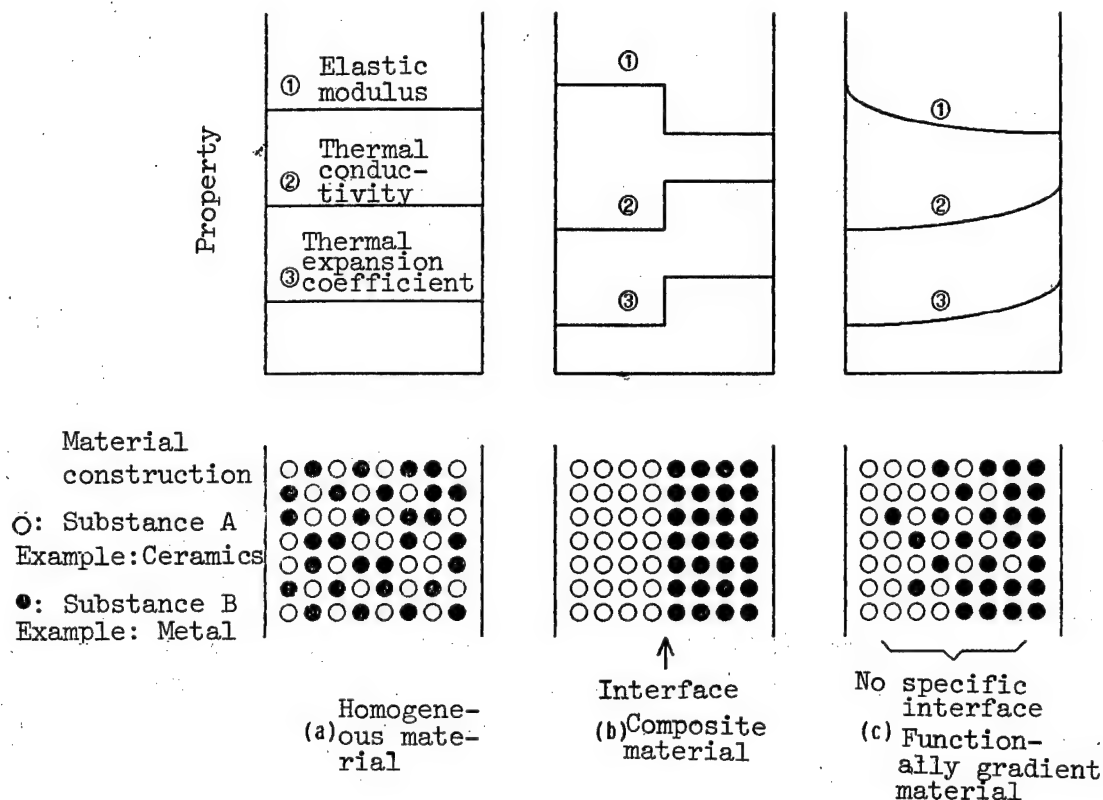


Figure 1. Sectional Construction of Various Materials and Changes in Their Internal Properties

example, the difference in thermal expansion coefficient among them causes a large thermal stress to be generated in the interface. Heating and cooling, once the conjugate, will not cause this stress to lead to fracture, but, when repeated, they will cause thermal fatigue. When a reaction occurs in the interface-peeling, falling and fracture in the surface layer occur due to the deterioration in interface strength resulting from changes with time, or, not going so far, problems will arise such as the deterioration in corrosion resistance due to the occurrence of cracks. At present, an attempt to change composition stagewise is being made with a view to control these problems with no satisfactory results.

These problems mainly result from the existence of a different phase interface, which implies that these problems can be solved by eliminating a different phase interface. How can a different phase interface be eliminated in an integral material in which materials completely different in properties, ceramics and a metal, for example, coexist? To cope with these problems, Japan has taken the lead in proposing the concept of a material with functions changed in succession by continuously controlling microscopic compositional elements to eliminate the boundary in the interior as shown in Figure 1 (c). In such a material, no sharp different phase interface exists and therefore, no large difference exists between ceramics and a metal. In other

words, dynamic, thermal and chemical functions are gradient continuously from surface to back of the material, which relaxes thermal stress and enables predetermined performance, such as thermal shielding quality and high thermal conductivity. This is a functionally gradient material.

## 2. Design of Functionally Gradient Materials and Their Production Technology

Technology for functionally gradient materials beginning with a new concept, methods for designing, synthesizing and evaluating properties of these materials are all unknown. In order to generate the above functionally gradient materials, multiple approaches are necessary but it will never be generated by a single research institute. In this context, following the research in fiscal 1986, a project titled "Research on Basic Technologies for Developing Functionally Gradient Materials To Relax Thermal Stress," based on Adjustment Works Expenses for Promotion of Science and Technology by the Science and Technology Agency, has been in existence since fiscal 1987. This project comprises three departments--material, design, material synthesis and property evaluation. A large number of universities, national research institutes and private corporations participate in each department of research. The following are descriptions of the outlines of these departments.

### 2.1. Material Design Department

The design of functionally gradient materials requires software which design their optimum gradient compositions and manufacturing method which are tailored to the actual working environment. This department is operated mainly by the Precision Research Institute, Tokyo Institute of Technology, and the CAE Center, Daikin Industries, Ltd. The results obtained here are used as sources for the material synthesis department.

For material design, it is necessary to know the optimum concentration gradient to continuously change compositions from ceramics to a metal. However, conventional material design is based on a homogeneous body, and a material comprising more than one type of material like a composite, if its properties are different between its surface and back, is generally not included, much less those in which properties change continuously.

As the first step, let us consider a plate in which the composition is continuously gradient only in direction of thickness as shown in Figure 2. An extremely thin portion of the plate interior (hereafter to be called a microcomplex) is a mixed body of ceramics and a metal, and the composition is homogeneous. Now, the portion close to ceramics is in the state where a metal has dispersed in the ceramics parent material, while the portion close to the metal is in the state where ceramics have dispersed in the metallic parent material.

The properties of this microcomplex depend upon the combination of ceramics and a metal and the configuration and distribution of a dispersed material. The combination of materials is determined by heat resistance and dynamic properties necessary. As the configuration of a dispersed material, a rotary

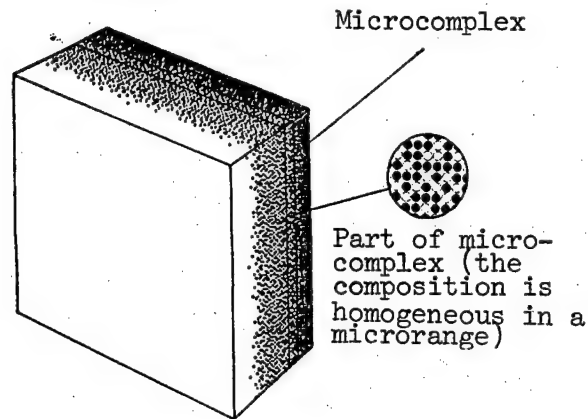


Figure 2. Construction of a Functionally Gradient Material  
(white portion, ceramics; black portion, metal)

ellipsoid is considered. By changing its axial ratio, it can be changed into a fibrous, a spherical or a plate-shaped one. Also, with a fibrous or a plate-shaped dispersed material, the orientation can be taken into account. From the above conditions, the homogeneous distribution is employed.

Elastic modulus, thermal conductivity and specific heat of microcomplexes can be regarded as those of the composite material using properties of ceramics and the metal. However, since strength and fracture elongation are difficult to obtain by theoretical calculation, measured values are used. According to the above process, the properties of the microcompound material are known.

Next, it is considered that a functionally gradient material, as a whole, comprises laminated microcomplexes with their composition progressively changed. Therefore, the thermal and dynamic properties of the functionally gradient material can be calculated as an aggregate of microcomplexes whose properties are known. The properties of the entire functionally gradient material with various concentration gradients are guessed by changing the combination of the thickness and the sequence of this microcomplex. Thus, an optimum concentration gradient to obtain a material with minimum thermal stress in the interior is found.

The design department plans functionally gradient materials while introducing many of these factors. Naturally, these calculated results are the primary approximation, and design precision should be improved by feedbacking the results of the property evaluation of functionally gradient materials synthesized, based on the design.

## 2.2. Material Synthesis Department

Next, it is necessary to establish technology for forming an integral material while continuously changing the composition of metallic and ceramics materials based on the optimum concentration gradient obtained by material design, i.e., a method for synthesizing a functionally gradient material actually possessing



predetermined functions. While various methods for obtaining such materials can be considered, the synthesis department of this project is conducting research on the four fields--(1) PVD and CVD, (2) particle injection, (3) thermal spray and (4) self-exothermic. For each approach, a study has been made on the process and requirements for functionally gradient materials, capable of generating predetermined properties without dispersion. With respect to any of these synthesis methods, small-size materials with a diameter of about 30 mm have been produced successfully, with the clarification of their thermal and dynamic properties being promoted. The following are their descriptions.

### 2.2.1. PVD and CVD

One method for synthesizing ceramics is vapor deposition, which includes physical vapor deposition (PVD) and chemical vapor deposition (CVD). PVD is a method involving evaporating a metal, synthesizing ceramics by introducing a reactive gas into the metallic vapor thus obtained, and depositing them on the substrate. On the other hand, CVD is one involving introduction of a mixed gas, containing metallic elements and metalloids and one which generates carbide and nitride into a reaction tube and depositing ceramics generated by heating the substrate. By either method, a functionally gradient material with the composition continuously changed from metals and metalloids to ceramics can be obtained. These methods are suitable for producing thin coating below 500  $\mu\text{m}$  thick with fine texture and subtle changes in composition. Each portion of a material obtained will be a mixed body of a molecular level. The Functional Property Research Division, National Research Institute for Metals, Science and Technology Agency, is conducting the synthesis of functionally gradient materials by PVD. With this approach, as shown in Figure 3, Ti, Cr, etc. in a water-cooled copper crucible are evaporated by plasma;  $\text{N}_2$  and  $\text{C}_2\text{H}_2$  gases are introduced into the metallic vapor thus obtained while changing their flow, and  $\text{Ti} \rightarrow \text{TiN}$ ,  $\text{Ti} \rightarrow \text{TiC}$  and  $\text{Cr} \rightarrow \text{CrN}$  are synthesized (the arrow ( $\rightarrow$ ) shows that the composition is changing continuously). With materials produced by this method, no crystal grains can be observed on an SEM observation level, depending upon producing conditions. As an example, Figure 4<sup>(1)</sup> (not reproduced) shows a sectional photo of a  $\text{Ti} \rightarrow \text{TiN}$  gradient composition film and impressions caused during a Knoop hardness test at portions. The substrate metallic portion, softer than ceramics, has larger impressions. The functionally gradient layer portion looks like a single phase, however, impressions becoming smaller as they are apart from the substrate show that the composition gradually changes.

The Metallic Material Research Institute, Tohoku University, is studying functionally gradient materials using CVD. The research group has assessed C with high heat resistance and is making an attempt of producing  $\text{C} \rightarrow \text{SiC}$  with a view to improving its oxidation resistance. They allow silane and carbide hydrogen to react in  $\text{H}_2$  gas while changing their mixing ratio, thereby obtaining  $\text{C} \rightarrow \text{SiC}$ .

Any method of PVD or CVD enables functionally gradient materials to be obtained, but they have different characteristics. PVD does not require heating of the substrate, but CVD does and such differences result in the difference in properties of materials obtained.



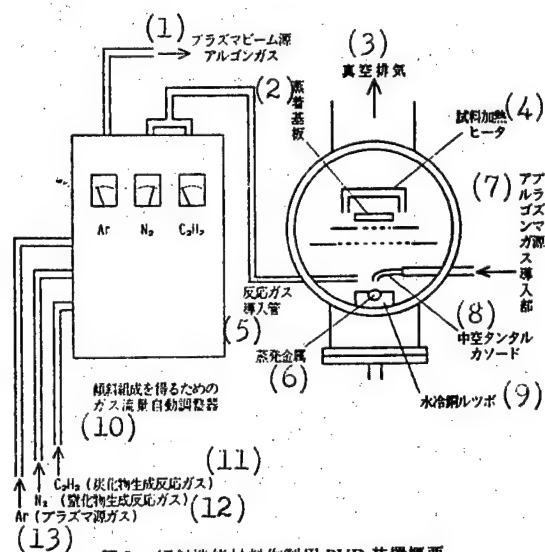


図3 傾斜機能材料作製用PVD装置概要.

Figure 3. Outline of a PVD Device for Use in Producing Functionally Gradient Materials

Key:

- |                                  |  |
|----------------------------------|--|
| 1. Plasma beam source argon gas  | 8. Hollow tantalum cathode   |
| 2. Vapor deposition substrate    | 9. Water-cooled copper crucible                                    |
| 3. Vacuum exhaust                | 10. Automatic gas flow adjuster for obtaining gradient composition |
| 4. Specimen heating heater       | 11. $C_2H_2$ (carbide generating reactive gas)                     |
| 5. Reactive gas introducing tube | 12. $N_2$ (nitride generating reactive gas)                        |
| 6. Evaporated metal              | 13. Plasma source gas  |
| 7. Plasma source argon gas inlet |  |

Sumitomo Electric Industries, Ltd. is currently studying PVD/CVD combination technology, based on the research results of the above two approaches, in order to make use of individual advantages and to supplement disadvantages. This group is producing functionally gradient materials with multiple layers of  $Ti \rightarrow TiC$ ,  $SiC \rightarrow C$ , etc.

Before the practical use of functionally gradient materials, it is necessary to conduct an actual environmental test in the end. However, a test under the above severe conditions naturally becomes large in scale. To cope with this, as a precursor to the actual environmental test, this group is developing a computer simulation program to obtain the standard of the thermal stability.

### 2.2.2. Particle Injection

Powder metallurgy is a popular method with respect to both ceramics and metals. It is conceivable to produce functionally gradient materials using this method by directly mixing ceramics particles and metallic powder while changing the composition and sintering the mixture obtained. The size of the configuration material, which is determined by the material powder, is  $0.1\ \mu\text{m}$  to several tens of micron meters, notably large when compared to vapor deposition. Materials are combined by chemical and physical combination.

The Department of Material Processing, School of Engineering, Tohoku University, prepared mixed powder of composition-changed ceramics particles and metallic powder, as the first step, and sintered this powder filled in a die in compositional order. With this method, the area and thickness of the material obtained is limited by the die.

Later, they conducted a study of particle injection involving filling powder directly into a die while controlling the quantitative ratio between ceramics and metallic powder. They produced a mixed body of  $\text{ZrO}_2$  and metals (stainless steel, Mo, Ni, etc.) using this method, compressed and sintered it, thereby obtaining functionally gradient materials. In this case, sintering temperature and the contraction of products after sintering, depend upon the composition ratio. The most important here is to balance these factors with an integral material. Figure 5<sup>(2)</sup> presents a typical figure of the texture of a functionally gradient material. This is a photo of the boundary between the two phases based on a photo of the texture of an actual functionally gradient material comprising  $\text{ZrO}_2$  and stainless steel. Also, a study is being made on a method for sintering in place using a laser while conducting particle injection; however, this method requires a severe limit of materials with area.

On the other hand, NKK Corp. has been conducting research on a thin film laminating method. With this method a slurry, consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and an Ni alloy, is first produced. Then, this slurry is made into thin films (green sheets) by the doctor blade method. These green sheets with different compositional ratios are laminated in compositional order and sintered. In this case, it is important that the slurry is spread thin and dried so that cracks may not be caused during production of green sheets and that well balanced contraction is produced during lamination sintering. In addition, this group is making a study of a method for producing functionally gradient materials by simultaneously depositing metals and ceramics powder, making use of plating, using an electrolyte in which ceramics powder floats.

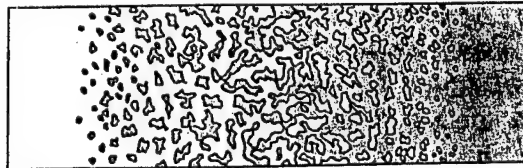


Figure 5. Texture of a Functionally Gradient Material Produced by the Powder Method<sup>(2)</sup>  
(Transferred from a texture photo of stainless steel  $\rightarrow$   $\text{ZrO}_2$ : black portion, stainless steel; white portion,  $\text{ZrO}_2$ )

### 2.2.3. Injection Method

This method enables functionally gradient materials to be obtained by injecting ceramics and metals while continuously controlling their ratio. The textures of materials obtained resemble those obtained by the powder method, but holes tend to remain, to some extent, since no pressurizing operation is conducted. The thickness depends upon injection time and, at present, the thickness enabling materials with few defects to be obtained is up to about 1 mm. With no sintering process, this method does not create a problem of sintering balance; furthermore, it uses no die, thereby offering an advantage of less limit with respect to the area of materials obtained.

The Texture Control Research Division, National Research Institute for Metals, is conducting research on dissimilar particle independent injection technology for injecting metals and ceramics while changing their compositional ratio using two injection guns. With respect to technology for controlling compositional ratios of individual portions of functionally gradient materials, a study is being made on the problem of the interruption between plasma jets to make dissimilar particles, independently injected with a homogeneous mixed body at a point and on the adhesion ratio of dissimilar particles, changeable depending upon injection conditions.

Nippon Steel Corporation is carrying out research on dissimilar particle simultaneous injection technology for injecting ceramics and metals while simultaneously supplying an injection gun with them. This method has dissimilar particles with different melting temperatures on one jet, so it is important that particles are fed at a position where temperature is optimum for a jet and dissimilar particles are well mixed into a jet.

### 2.2.4. Self-Exothermic Reaction Method

This is a method for sintering and molding making use of exothermic resulting from chemical reaction between component powder. Therefore, the application of this method is limited to producing compounds with high heat reaction. Some of those compounds have high melting points, creating no problem in terms of heat resistance. Also, it is characteristic for them to be sufficient without outside heat necessary for sintering. For example, mixing Ti and B powder and igniting to trigger a reaction, cause the two to react with each other and heat of reaction, when  $TiB_2$  is generated promotes reaction in remaining powder. Temperature of the entire specimen, then, reaches as high as above 3000 K, causing  $TiB_2$  generated by this heat to be sintered.  $TiB_2$  has a melting point of 3173 K and is extremely high in heat resistance in a nonoxidizing atmosphere. In this field, research is being conducted on materials with gradient composition from metals, such as Cu and Ni, with good thermal conductivity to  $TiB_2$  and  $TiC$ . The problem with much metals is largely different from that of the portion with much Ti+B and Ti+C. The portion with much Ti, B and C, temperature becomes excessively high, sometimes causing bulky crystal grains of sintered bodies or remaining holes, resulting from the gasification of mixed metals.

The Functional Ultimate Material Research Center, Science and Technology Research Institute, Osaka University, has been conducting a detailed study of the reaction process with respect to gradient composition materials, such as

Cu→TiB<sub>2</sub> and Ni →TiC systems, in order to solve the above problems. They are studying technology for premixing, according to their composition, a proper amount of TiB<sub>2</sub> and TiC which have completed reaction with material mixed powder in order to suppress the generation of excessive heat reaction. TiB<sub>2</sub> and TiC which have completed reaction serve here as a diluent against heat of reaction to control a rise in temperature.

This method provides a large calorific value, which alone cannot lead to obtaining sintered bodies without holes, so HIP is also used. However, a method using HIP for molding is limited in size of materials obtained.

To cope with this, the Government Industrial Research Institute, Tohoku, aiming for its practical use in the future with regard to obtaining large-size materials, is studying low pressure molding technology using hydrostatic pressure. With material systems, research is being carried out on TiB<sub>2</sub>-Cu-system functionally gradient materials.

### 2.3. Evaluation Department

With functionally gradient materials, it is difficult to know their properties by means of ordinary measuring methods since thermal and dynamic properties have changed in the interior. For example, dynamic properties of ceramics largely differ from those of metals, which makes it difficult to evaluate them with the same testing method.

In an ordinary tensile test, a plane stress is applied to a specimen; however, the same condition cannot be set with functionally gradient materials since elastic modulus has changed in the interior of specimens. The evaluation department needs to establish technology to find these properties and create a data base to feedback to the design department.

The Material Strength Research Institute, Tohoku University, has developed a unique strength test method, an improved version of a small punch test, while the School of Engineering, Shizuoka University, is studying a method for measuring thermal properties such as thermal diffusivity. In addition, a study of testing of fracture toughness and thermal impact is being made and, parallel to the above, each evaluation institute measures materials from the synthesis department. The National Aerospace Laboratory, Science and Technology Agency, structures a data bank with respect to data obtained and feeds it back to the design department.

## 3. Applications of Functionally Gradient Materials to Other Sectors

As stated so far, current projects involving functionally gradient materials are focusing on the relaxation of thermal stress. The concept of being functionally gradient is expected to result in a great effect not only on the thermal stress but on the following sectors.

### 3.1. Materials for Medical and Organic Use

For artificial teeth bones and joints, inactive materials, such as apatite, alumina and stainless steel with good biocompatibility are used. These

materials, however, have such disadvantages as being heavy in weight and short of ductility when compared to natural ones. These problems can be answered by functionally gradient materials. Figure 6<sup>(3)</sup> presents the structure of an artificial tooth with gradient composition which is currently considered. In order to increase biocompatibility, the fang is made of porous apatite and the interior is constructed close with a view to high strength. The exposed section of the tooth is made of high-hardness ceramics and the central section of high-toughness ceramics.

With artificial bones, too, high biocompatibility can be obtained by adopting a design, consisting of the exterior and the interior of porous apatite and a material with light weight and high strength to reinforce the medium. With respect to artificial joints, flexible joints can be designed, so as for cartilages, cords and bands to be conjugated or to combine an artificial material with an organic one.

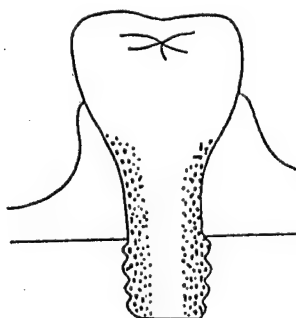


Figure 6. Artificial Tooth Mode of a Functionally Gradient Material<sup>(3)</sup>

For artificial organs, biocompatibility (no rejection, no blood agglutination and no occurrence of thrombus), flexibility, high reliability and functionality (selective permeability of artificial kidneys) are required. Materials with such multiple functions are likely to lead to the practical use of artificial hearts, artificial kidneys and adjustable artificial crystalline lenses by continuously polymerizing and synthesizing various gradient-composition polymeric materials.

### 3.2. Electric, Magnetic and Optical Functions

Gradient composition control technology will enable the miniaturization and improved functions of electronic parts.

#### 3.2.1. Electroceramics

With sonars and sensors of supersonic diagnosis apparatuses, acoustic matching with measuring objects creates a problem. To cope with this, these instruments are used by gluing matching materials, such as metals, plastic and rubber, and absorbers to them. However, they will encounter failure due to the deterioration

of adhesive bonds, the occurrence of spurious--resonance and oscillation with unintended frequencies--due to acoustic discontinuation and a decrease in S/N ratio. These problems can be solved with the use of functionally gradient mount.

Materials with higher functions can be developed by slanting the internal composition of supersonic piezoelectric transducers and ceramics filtering elements and by providing optimum distribution of piezoelectric constants and temperature coefficients. In addition, a new piezoelectric material with a gradient composition construction, combined with organic piezoelectric material can be considered.

For monitoring temperature and gas temperature in the hot and corrosive environment, it is sometimes necessary to install a sensor on the metallic base via an insulator, or, for detecting the flow rate and concentration of a fluid, to install sensors in the pass to fetch signals. In such environment, it is difficult to use a plastic insulator or an adhesive bond, so it is necessary to install a sensor in the metallic base or the metallic tube via insulating ceramics. Such a construction is likely to cause a gap between metals and ceramics due to the difference in thermal expansion coefficient. In such cases, as shown in Figure 7(3) (a), the above problems can be solved by using mount integral ceramics or, as shown in Figure 7 (b), by using a functionally gradient sensor with composition, such as metal (the tube in the pass)→ceramics (insulator)→metal (sensor).

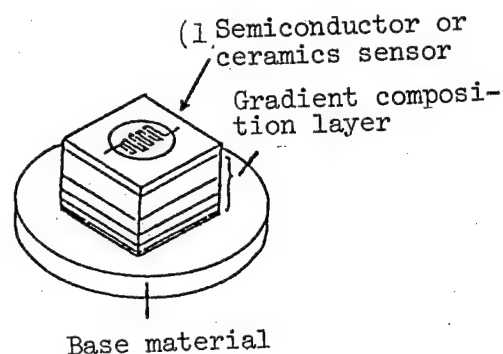
### 3.2.2. Semiconductor Device

Silicon cannot be used for optoelectronic devices and semiconductor devices. Also, since silicon and compounds are different in lattice constant, a compound semiconductor cannot be directly grown on the silicon substrate. However, the likelihood of making the portion, as much as necessary, into a compound semiconductor by slanting the composition, using MOCVD and MBE, is likely to lead to the completion of an electronic device with high performance and low price.

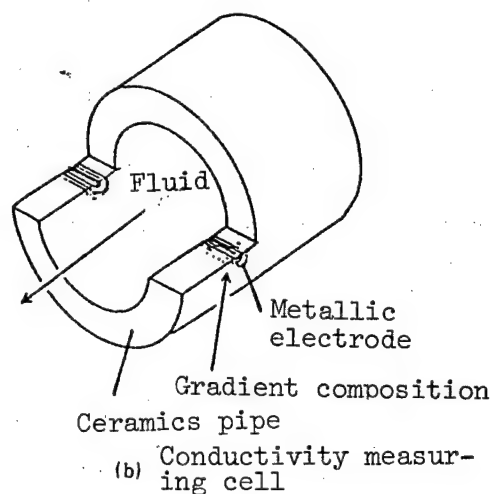
### 3.2.3. Magnetic Applications

With magnetic disk memories, vertical recording is beginning to be put to practical use. A magnetic thin film, a recording medium, has double design consisting of a film with soft property and one with hard property on it. A magnetic material deteriorates in properties when a stress is applied, but this can be improved by slanting the film composition

Iron cores of permanent magnets and electromagnets for use in motors and NMRs are required high saturation magnetic flux densities. Configurational device will allow portions of these iron cores requiring the use of precious alloys to be minimized. Low-priced alloys are used for portions which allow low magnetic flux densities. Low-priced magnets with high performance can be produced by slanting the composition according to magnetic flux densities.



(a) Mount integral sensor



(b) Conductivity measuring cell

Figure 7. Functionally Gradient Material Applied Sensor<sup>(3)</sup>

#### 3.2.4. Optical Function

The distribution of refractive indexes is not uniform with multimode fibers and GRIN lenses, those in the center being high and those in the periphery low. With laser rods of a glass laser, the concentration distribution of ND dope is controlled, thereby making the luminous and cooling efficacy optimal. New optical parts and optical memory can be constructed by controlling the composition more actively with these materials to cause a major change in refractive indexes or by generating materials with an electro-optical effect and a magneto-optical effect in the interior of optical materials. In addition, it will be possible to design and produce large-output laser rods incorporating a thermal stress relaxation function.

#### 3.3. Chemical Function

Studies are under way on Cl chemistry involving synthesizing petrochemical materials from compounds with relatively simple constructions using high-performance films and catalysts, a chemical synthesis method which promotes

Table 1. Functionally Gradient Material Applied Fields Other than Thermal Stress Relaxation (3)

<u>Expected Function and Effect</u>	<u>Applied Field</u>	<u>Property and Composition</u>
Nuclear function	Materials for the first wall and the periphery (limiter, diverter) Electric insulating material (for toroidal structure and superconductive materials use) Aperture material for use in plasma instrumentation and control	Radiation resistance, heat resistant stress, low $\frac{1}{2}$ quality, electric insulation quality  Translucency, radiation resistance
Bonding function	Ceramics engine Wear resistant mechanical parts Heat resistant mechanical parts Corrosion resistant mechanical parts Other mechanical parts	Ceramics and metals Glass and metals Plastics and metals Dissimilar metals Dissimilar ceramics Dissimilar plastic
Medical, vital functions These functions are expected to improve biocompatibility and reliability more than conventional materials	Artificial teeth Artificial bones Artificial joints Artificial organs	Control of ceramics hole distribution Ceramics and plastic Ceramics and metals Gradient composition control for biomedical organic materials
Electromagnetic function This function enables improved properties, light weight and miniaturization.	Ceramics filter Ceramics oscillator Supersonic piezoelectric transducer Magnetic disk Permanent magnet, electromagnet	Gradient composition of piezoelectric substance Gradient composition of magnetic substance Gradient composition of metals Gradient composition of compound semiconductor

Continued on following page



Three-dimensional composite electronic parts

Compound semiconductor

Mixed IC

Long life heater

Sensor

Improved measuring  
precision, measuring  
under harsh environment

Mount integral sensor

Acoustic sensor well matching with media

Supersonic diagnosis device

Sensor with spatial distribution in  
sensitivity

Gradient composition between sensor  
materials and mount materials  
Gradient composition of piezoelectric  
substance

Optical function

Improved performance

High performance laser rod

Large aperture PRM lens

Optical disk

Gradient composition of optical materials

Chemical function

Functional polymeric film catalyst

only specific reaction by means of a laser, and a bioreactor applying fermentation and gene recombination technology. Functionally gradient material technology can be applied to films, catalysts and reaction vessels for use in these studies. Table 1<sup>(3)</sup> shows a summary of effects expected of functionally gradient materials when they are used in fields other than thermal stress relaxation.

#### 4. Conclusion

Research on functionally gradient materials has just been initiated. Therefore, only a portion has currently been studied, mainly of the relaxation of thermal stress. In the synthesis department, however, all methods have successfully produced functionally gradient materials, with the clarification of their properties being made. Their practical implementation will require a study of the process for large-size materials and materials with complex shapes. In addition, there remain problems of oxidation resistance and changes in properties with extended use of these materials at high temperature. With materials themselves already available, these problems will be solved in succession.

It is deemed that the application range, other than the relaxation of thermal stress, is considerably wide. However, a large number of factors must be taken into account, when only the relaxation of thermal stress is intended. Therefore, the expansion of the application range to other fields will necessarily need more factors to be considered. After introducing these factors, computer-aided material design will be powerful means for obtaining optimum gradient compositions corresponding to individual purposes, via the complex material design process. It is considered that materials with high functions or those with properties not found in conventional counterparts can be created by checking properties of materials synthesized on the basis of material design and by feeding them back to material design.

This research is conducted as a project by the Science and Technology Agency and a group of researchers from industry, government and academia who are interested in this field and offer workshops and fact-finding tours. Those interested are required to contact: 105 Functionally Gradient Materials Research Group 3F, Toranomon Kotohira Kaikan Building, 1-2-8, Toranomon, Minato-ku, Tokyo (phone no. 03-503-4681 FAX No. 03-597-0535)

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## Ceramics Nanocomposites, Ceramics Fine Composites

906C7532E Tokyo KYOKUGEN KANKYO YO TAINETSU FUKUGO ZAIRYO in Japanese  
20 Jan 90 pp 69-76

[Article by T. Hirai and T. Goto, Metallic Materials Research Institute, Tohoku University: "Nanocomposites; Fine Composites; In-Situ Combining Method; Design of CVD Fine Composites"] [This article is a paper described in the Japan Society of Metals Magazine Vol 28 (1989), No 12 transcribed after correcting part of format, such as the caption, etc.]

### [Text] 1. Introduction

Carbon fiber reinforced plastic (FRP) has recently come to be in the spotlight as a material for use in aerospace related fields, such as supersonic aircraft and space stations, which is largely attributable to the refining of the production process. Along with the working environment of materials becoming harsh and their production process improving, superior composite materials have come to be developed, going so far as to be said that it is composite materials that support advanced science and technology. This trend is particularly remarkable in the field of ceramics, which is enabling the production of ceramic fiber reinforced ceramics (CFRC). With respect to the improvement in the mechanical properties of ceramics composites, remarkable progress has been seen in recent years. For example, with carbon long fiber combined  $\text{Si}_3\text{N}_4$ , the room temperature strength and high temperature fracture toughness value reach 690 MPa and 29  $\text{MPa}\cdot\text{m}^{1/2}$  (at 1470 K), respectively<sup>(1)</sup>, implying that it is close to the practical phase. A composite material consists of a parent phase and a dispersed phase, the size of the latter generally being  $\mu\text{m}$  order. On the other hand, ceramic composites (ceramic nanocomposites), which have an extremely small dispersed phase several to 10 nm in size and have the composite texture controlled on a nm level, have been catching attention in recent years. With nanocomposites, it is expected that new properties, which would be unthinkable under the normal combination law, will be manifested. In addition, one of the authors (Hirai) has recently disclosed ceramic fine composites dispersed with various elements other than the ceramic substances<sup>(3)</sup>. The dispersed phase comprising composites is ordinarily considered as a substance, but when it comes to fine composites, factors such as crystal shape, crystal orientation, grain boundary and defects, are regarded as a dispersed phase.

Table 1. Comparison among Hybrid Materials, Fine Composites and Composites (3)

	Hybrid Material	Fine Composite	Composite
Combination purpose	Substance	Other factors	Substance
Combination method	Phase bonding	Phase separation	Phase bonding
Combination format	Atomic/molecular-level combination	Nanosize dispersion	Nanosize mixing
Texture control area	Below several nanometers	Several to several tens of nanometers	$\mu\text{m}$ to mm
Parent/dispersed phase combination	Atomic/molecular combination	Grain boundary	Grain boundary
Combination of cavity	Difficult	Possible	Possible
Synthesis method	Physical, chemical	Physical, chemical	Mechanical
Synthesis temperature	Low	High	High
Synthesis system	Few	Multiple	Multiple
Making materials into thin films	Possible	Possible	Possible
Enlargement of materials	Difficult	Possible	Possible
Correspondence to the combination law	Impossible	Impossible, possible	Possible

The word "hybridization" or "hybrid material" similar to fine composites has recently been used in the physical and chemical sectors<sup>(4)</sup>. Table 1 compares "fine composites" and "hybrid materials" mentioned in this article with conventional "composites." A fine composite is positioned, as shown in Table 1, between hybrid materials and conventional composites, while it differs from these materials in terms of a combination method or a combination form. In other words, since fine composites are related to the combination and slanting of compositions and functions, their material design is different from conventional material design methods<sup>(5)</sup>.

As stated thus far, a new movement has recently been seen with ceramics composites. In this context, this article presents the concepts of "nanocomposites" and "fine composites" of ceramics and describes their synthesis methods, constructions and properties.

## 2. Nanocomposites

Using the solution-sol-gel method, Roy synthesized composite ceramics with dispersed phases as large as several to several tens of nanometers and are generically named nanocomposites<sup>(2)</sup>. For the solution-sol-gel method, please refer to other explanations<sup>(6)</sup>. Table 2<sup>(6)</sup> shows examples of nanocomposites synthesized by the solution-sol-gel method. Of nanocomposites in Table 2,  $\text{SiO}_2+\text{AgCl}$  and  $\text{Al}_2\text{O}_3+\text{Ni}$  are expected to be used as a photochromic material and a structural material (hardness, 20 MPa; fracture toughness value, 5-10  $\text{MPa}\cdot\text{m}^{1/2}$ ), respectively.

Table 2. Examples of Synthesizing Nanocomposites by the Solution-Sol-Gel Method<sup>(6)</sup>

Noncrystalline parent phase + noncrystalline dispersed phase	Noncrystalline parent phase + crystalline dispersed phase	Crystal parent phase + crystal dispersed phase
$\text{SiO}_2+(\text{AlOOH})_n$	$\text{SiO}_2+\text{AgCl}$	$\text{Al}_2\text{O}_3+\text{Ni}$
+ $\text{AlPO}_4$	+CdS	+Pt
+ $(\text{NdOOH})_n$	+ $\text{BaSO}_4$	+Cu
	+ $\text{PbCrO}_4$	$\text{ZrO}_2+\text{Cu}$
	+Cu	+Pt
	+Ni	

On the other hand, with respect to the application to electromagnetic materials, Newnham<sup>(7)</sup> has reported a guideline to material design. He has stated that geometric connectivity of a parent phase and a dispersed phase is particularly important as factors determining composite properties. In addition, mentioning the advantages and the disadvantages of nanocomposites, he has implied that, with ferromagnetic and ferroelectric ceramics, when a dispersed phase is below

the size of the magnetic domain, it behaves like single magnetic domain particles which remarkably increase coercive force, and, when it is below about 20 nm, it becomes superparamagnetic [phonetical] (dielectric) and able to change the sense of a spin with a small magnetic field (electric field). He also points out that the periodicity and symmetry property of a dispersed phase are important factors in determining composite properties. For the detail of design of these materials, refer to the original paper<sup>(7)</sup>.

### 3. Fine Composites

Conventional "combination" is mixing of substances A and B. Along with the sophistication of material synthesis approaches in recent years, the synthesis of more controlled (finer<sup>(3)</sup>) materials has become possible. With conventional ordinary composites, it used to be indispensable for factors to determine properties having the size and shape of the dispersed phase and for the dispersed phase to disperse homogeneously. With fine composites recently advocated, however, a dispersed phase is not limited to a fixed phase but to a large number of factors<sup>(3)</sup> in Table 3.

Table 3. Factors Considered as Dispersed Phases of Fine Composites<sup>(3)</sup>

Factors for Making Complex	Content
Form of dispersed phase	Sphere, foil, thin layer, needle, fiber
Type of dispersed phase	Solid phase, liquid phase, vapor phase (void, cavity)
Structure of parent phase and dispersed phase	Crystalline, random layer structure, noncrystalline
Crystal completeness of parent phase and dispersed phase	No defect, lattice irregularity, lamination defect
Matching quality and orientation of parent phase and dispersed phase	Conformability-unconformability, orientation-no orientation
Dispersion status of interface dispersed phases of parent phase and dispersed phase	Formation reactive products and occurrence of stress by chemical reaction
	Homogeneity-inhomogeneity, continuation-discontinuation

For example, fine composites include those with substances having the same chemical composition, materials with areas different in crystal structure and crystal orientation dispersed, those with stacking faults and lattice defects dispersed, those with gaps dispersed and those with residual stress dispersed. A nanocomposite with an extremely small dispersed phase is part of a fine composite with size as a factor. In other words, a fine composite can be

called an ultimate composite in that it controls not only the shape and size of a dispersed phase but every parameter, such as microstructure and properties.

Functionally gradient fine composites are a material which has been developed on the basis of fine composites or nanocomposites<sup>(8)</sup>. In the case of a general composite, the properties are the same with the entire material. However, a material with properties on one side completely different from the other can be produced by continuously controlling the factors for being complex. Such materials are called functionally gradient composites<sup>(8)</sup>.

#### 4. In-Situ Combination Method

Fine composites generally cannot be synthesized by the phase bonding method<sup>(9)</sup> for the production of ordinary composites, so it becomes necessary to adopt the in-situ combination method<sup>(9)</sup>.

Figure 1 illustrates the concept of the in-situ combination method. In the figure, B is a dispersed phase in ordinary composites, corresponding to dispersion factors in fine composites. Table 4 shows a summary of various in-situ combination methods<sup>(3)</sup>. A homogeneous material, starting in the in-situ combination method, is possible in any state of solid, molten substance, fluid and gas and the difference in the following processing enables multiple methods to exist. The following are brief descriptions of individual examples.

Table 4. In-Situ Combination Method Used for Producing Ceramics Nanocomposites<sup>(3)</sup>

Solid treatment	Partial crystallization
	Phase splitting
	Intergranular reaction
	Thermal decomposition of organic metallic compound
Molten metal treatment	Solidified deposition
	Eutectic reaction (one-way solidification)
Liquid treatment	Sol/gel
	Coprecipitation
	Water calory
Gas treatment	PVD
	CVD

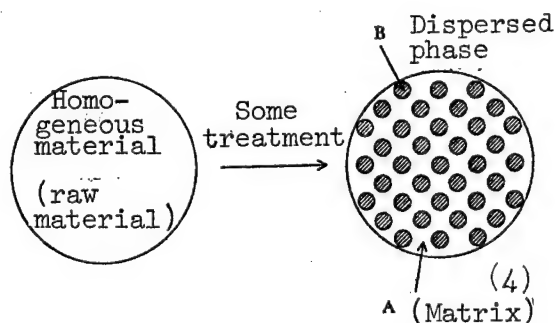


Figure 1. Concept of Synthesizing Nanocomposites by the In-Situ Combination Method<sup>(3)</sup>

#### 4.1. Processing of Solids

As an example of "partial crystallization," there is one of cuttable glass developed by US Corning Corp<sup>(10)</sup>. With this glass, a plate-shaped mica crystal, about  $-20\text{ }\mu\text{m}$  thick, was deposited in the postmelting thermal processing process. Cracks stopping in the mica during cutting prevents them from advancing into the interior. No detailed report has been made on the size effect of plate-shaped mica, a dispersed phase.

As an example of phase splitting, there is a Spinodal decomposition of  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_3$  system glass. With this system, the structure, in which  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$  glass phase and  $\text{SiO}_2$  glass phase of several to several tens of nanometers in size are entangled with one another, can be observed<sup>(11)</sup>.

Representative examples of those making use of "intergranular reaction," are electronic ceramics, such as various thermistors and varistors. Figure 2 presents an example of the relationship between the average grain size and the varistor voltage with a  $\text{ZnO}$  varistor<sup>(12)</sup>. Since the grain boundary becomes highly electrically resistant, the smaller the grain size, the higher the varistor voltage. In addition, a thermistor has been developed in which the interior of grains become semiconductors and the grain boundary an insulator when  $\text{Mg}$  and  $\text{Ca}$  are added to  $\text{BaTiO}_3$  system materials and the grain boundary alone is oxidized after sintering<sup>(13)</sup>.

As an example of "thermal decomposition of organic metallic compounds," one involving the production of textures of  $\text{SiC}$ , etc. is available<sup>(14)</sup>. First of all, the starter 'polycarbosilane' was spun into a fiber, which was then sintered to produce an  $\text{SiC}$  fiber Nicalon<sup>(15)</sup>. The fiber has a diameter of from  $10$  to  $15\text{ }\mu\text{m}$  and a tensile strength of about  $3000\text{ MPa}$ . Figure 3 presents the microstructure of a section of this fiber. The parent phase of the fiber contains amorphous  $\text{SiC}$  excess carbon, and partially contains the  $\text{Si-O}$  combination. This parent phase contains floating carbon of about  $1\text{ nm}$  in diameter and  $\beta$  type  $\text{SiC}$  crystals. In addition,  $\text{Si-O}$  bond on the surface exists in quantity<sup>(16)</sup>. It is deemed that an  $\text{SiC}$  fiber being high in strength also result from its being a nanocomposite shown in Figure 3<sup>(17)</sup>.



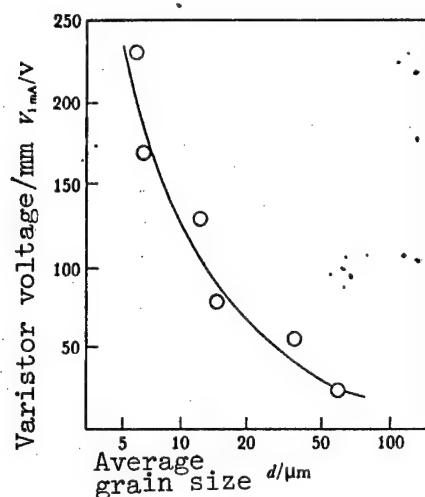


Figure 2. Relationship Between the Average Grain Size and Varistor Voltage in ZnO Varistor<sup>(12)</sup>

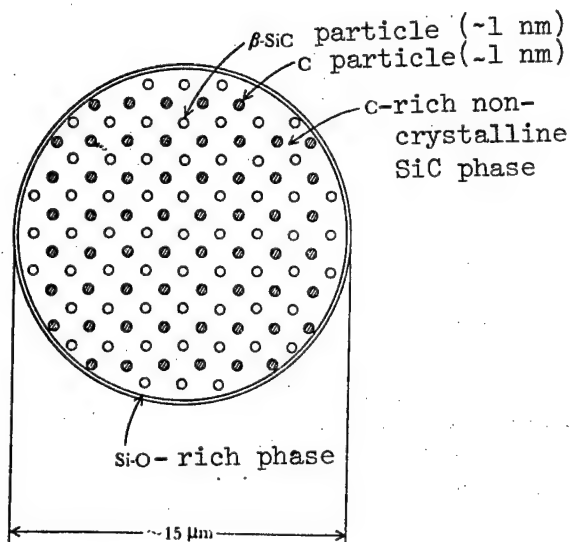


Figure 3. Typical Figure of the Sectional Structure of an SiC Fiber

#### 4.2. Treatment of Molten Substances

As examples of "solidified deposition," various liquid phase sintered bodies can be cited. For example, being sintering resistant,  $\text{Si}_3\text{N}_4$  needs assistance and the addition of  $\text{MgO}$ , etc. is effective, while at a sintering temperature

of 1870 K, molten Mg-silicate is generated, thereby forming an intergranular phase during cooling. In other words, this type of sintered body can be regarded as a composite of  $\text{Si}_3\text{N}_4$  particles and silicate intergranular phases. With respect to an in-situ composite<sup>(18)</sup> making use of phase separation in the solidification process, a large number of research examples have been reported. For example, one-way solidification of a molten substance with eutectic composition of the Ni radical-TaC system enables an in-situ composite with TaC dispersed fibrous in the parent phase to be obtained<sup>(19)</sup>. Figure 4 presents the relationship between the interfiber distance and the cooling rate. The interfiber distance decreases and the fiber dispersion density increases as the cooling rate increases. The strength of this in-situ composite increases as fiber dispersion density increases. For example, the maximum tensile strength at 1270 K increases from 152 MPa to 172 MPa when the interfiber distance decreases from 27 to 7.2  $\mu\text{m}$ .

Cermet, a composite of ceramics and metals, is one of the processes making use of solidification deposition. For example, WC-Co system cermet can be regarded as a quasi-binary system and it is known that a notable quantity of WC melts at above the liquidus line and that, when cooled, unmelted WC plays a role of nucleus for generating crystal particles<sup>(20)</sup>.

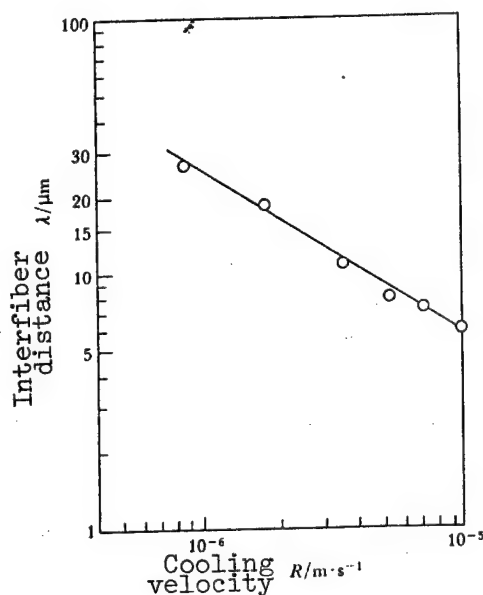


Figure 4. Relationship Between Cooling Velocity and Interfiber Distance of Ni Radical-TaC System In-Situ Composite

#### 4.3. Treatment of Liquids

The synthesis of composites by "sol-gel" has been described in the previous section.

"Coprecipitation" is a method involving homogeneously mixing individual components in the state of aqueous solution and depositing the mixed components as solid phases, making use of changes in the solubility caused by pH and temperature. For example, coprecipitates with various  $\text{MgO}/\text{Al}_2\text{O}_3$  ratios can be obtained by making an aqueous solution of  $\text{MgCl}_2$  and  $\text{AlCl}_3$  and by controlling pH<sup>(21)</sup>. Heating the coprecipitates to several hundreds of K enables composite fine particles to be obtained. No detailed report has been made on the fine particles.

As an example of composites by "water calory," the synthesis of  $\text{Al}_2\text{O}_3$ - $\text{HfO}_2$  fine particles can be cited<sup>(22)</sup>. First, Hf and Al are melted in a vacuum arc furnace to produce an  $\text{HfAl}_3$ -Al alloy. This alloy and distilled water are sealed into a platinum capsule, and endures hydrothermal treatment at a pressure of 100 MPa and a temperature of 670 to 970 K. Since hydrothermal oxidation of Al proceeds much faster than  $\text{HfAl}_3$  of the same condition, the hydrothermal oxidation of an alloy with  $\text{HfO}_2$  dispersed in Al, enables composite fine particles with  $\text{HfO}_2$  dispersed in  $\text{Al}_2\text{O}_3$  to be obtained. The grain size of  $\text{Al}_2\text{O}_3$  is several micrometers and the one of  $\text{HfO}_2$  10 to 20 nm.

#### 4.4. Treatment of Gases

The treatment of gases can be roughly divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD). Table 5 shows a summary of examples of synthesizing nanocomposites by PVD and CVD reported so far. While, with ordinary "composites," the form of dispersed phases is spherical or fibrous (whisker, etc.), nanocomposite textures of fine composite films obtained by PVD and CVD, take various forms as shown in Figure 5<sup>(55)</sup>. These nanocomposite textures undergo changes according to production conditions and the type of material gases.

PVD includes various methods of sputtering, ion plating, vacuum deposition, etc. and attempts at producing nanocomposite films are carried out mainly by sputtering. Since a target material is repelled in atomic and molecular size, the use of multiple targets or an alloy target enables nanocomposite films to be produced with ease. Also, introducing a reactive gas during sputtering and allowing a sputtering substance to react with the gas (reactive sputtering) enable various ceramic nanocomposite films to be synthesized.

As an example of a nanocomposite film produced by PVD whose construction and properties have been examined, a Co-Cr-C film can be cited<sup>(42)</sup>. It is reported that, when a Co-Cr film prospective as a vertically magnetized film is produced by sputtering magnetic properties, such as saturation magnetization and a coercive force, it can be improved by co-sputtering carbon. This is true because the addition of carbon causes a Co-Cr film to be divided into Co-rich phases and Cr-rich phases, resulting in remarkable magnetic anisotropy of individual phases. The improvement in magnetic properties is most remarkable where a carbon content is 0.25 mass percent. As shown in Figure 6, a TEM observation has made it clear that both Co-rich phases and Cr-rich phases are separated to be columnar when their diameters are several tens to several hundreds of nanometers. It is a good example of improved properties by making the film nanocomposite.

母相(1)	分散相(2)	型(3)	(4) サイズ (nm)	(5) 性質 (機能)	(6) 文献
[PVD]					
SiO <sub>2</sub>	WSi <sub>2</sub>	f	100	(11) コンデンサー	23
SiO <sub>2</sub>	MoSi <sub>2</sub>	f	200~500	(12) 半導体デバイス	24
SiO <sub>2</sub>	void	a	(7) 数~数10	低誘電率化 (13)	25
ZnS	Mn	f	150	(14) 光学素子	26
CoCr	polyethylene	a	25	垂直磁化膜 (15)	27
Al <sub>2</sub> O <sub>3</sub>	Pb	a	10~50	(16) 電気抵抗 (PTC)	28
Ni	Si	f	10	透光性 (遠赤外) (17)	29
Si	Nb	a	10~20	(18) 超伝導化	30
teflon	Au	a	10~100	着色フィルム (19)	31
SiO <sub>2</sub>	Au	a	7	(20) 導電性	32
In	InO <sub>3</sub>	f	10	光記憶 (21)	33
Ag	polymer	a	10~100	(22) 電気光学の性質	34
polymer	Au	a	10~20	着色フィルム (19)	35
SiO <sub>2</sub>	Ag	a	6~9	導電性 (20)	36
polymer	Au	a	1~7	(23) 絶縁耐圧	37
polymer	Au	a	10~120	光学応答性 (24)	38
BN	Fe, Co	a	1~30	(25) 磁性特性	39
polymer	Ag	a	20~40	半導体 (26)	40
SiO <sub>2</sub>	Fe	a	2~5	(27) 磁気記憶体	41
Cr-Co	C	a,c	(8) 数10~数100	垂直磁化膜 (15)	42
[CVD]					
C	SiC	b	(7) 数~数10	(28) 耐酸化	43
Si <sub>3</sub> N <sub>4</sub>	TiN	a,d	(7) 数~数10	(29) 断熱化	44
Si <sub>3</sub> N <sub>4</sub>	BN	f	(9) 数100	透明化 (30)	45
Si <sub>3</sub> N <sub>4</sub>	C	a	数100 (9)	(31) 耐電化	46
SiC	TiC	a,d	(8) 数10~数1000	高剛化 (32)	47
SiC	C	a,c	数10~数100	(33) 遮熱性	48
BN	TiN	a	3~5	耐層剥離性 (34)	49
SiO <sub>2</sub>	Si	f	1~2	(35) パッシベーター (半導体)	50
Fe, Ni	FeB <sub>2</sub> , NiP <sub>2</sub>	a	数10~数100	高強度化 (36)	51
Ta <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	a	1000	(37) 電気光学, ガスセンサー	52
SiO <sub>2</sub>	Si	a	10~20	半導体デバイス (2)	53
TiO <sub>2</sub>	SnO <sub>2</sub>	a	10~50	(38) センサー	54

Table 5. Examples of Synthesizing Nanocomposites by Gas Treatment

Key:

- |                                       |                                     |
|---------------------------------------|-------------------------------------|
| 1. Parent phase                       | 23. Dielectric pressure resistance  |
| 2. Dispersed phase                    | 24. Optical responsability          |
| 3. Type                               | 25. Magnetic property               |
| 4. Size                               | 26. Semiconductor                   |
| 5. Property (function)                | 27. Magnetic storage substance      |
| 6. Literature                         | 28. Oxidation resistance            |
| 7. Several to several tens            | 29. Ability of heat insulation      |
| 8. Several tens to several hundreds   | 30. Ability of making-transparent   |
| 9. Several hundreds                   | 31. Ability of making conductive    |
| 10. Several tens to several thousands | 32. Ability of increasing toughness |
| 11. Condenser                         | 33. Ability of thermal shielding    |
| 12. Semiconductor device              | 34. Layer peeling resistance        |
| 13. Low conductivity                  | 35. Passivator (semiconductor)      |
| 14. Optical device                    | 36. Ability of increasing strength  |
| 15. Vertically magnetized film        | 37. Electro-optics, gas sensor      |
| 16. Electric resistance               | 38. Sensor                          |
| 17. Translucency (far infrared)       |                                     |
| 18. Superconductivity                 |                                     |
| 19. Colored film                      |                                     |
| 20. Conductivity                      |                                     |
| 21. Optical storage                   |                                     |
| 22. Electro-optical property          |                                     |

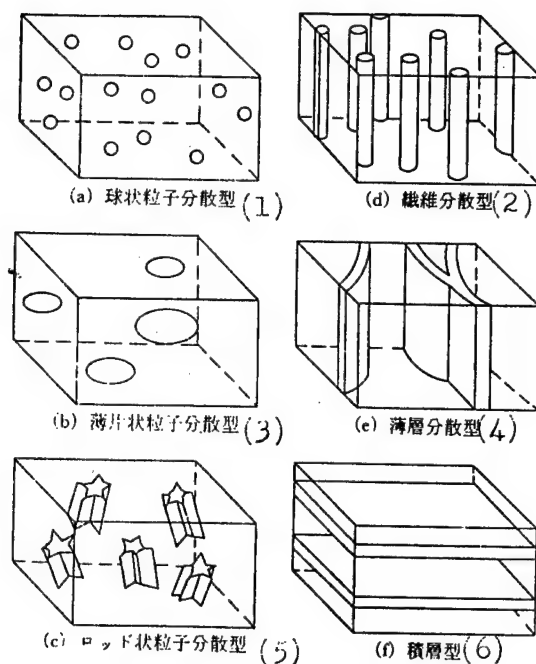


Figure 5. Nanocomposite Textures of Various Fine Composite Films<sup>(55)</sup>

Key:

1. Spherical particle dispersed type
2. Fiber dispersed type
3. Foil-shaped particle dispersed type
4. Thin layer dispersed type
5. Rod-shaped particle dispersed type
6. Laminated type

With CVD, fine composites can be synthesized with ease with the codeposition process using a hypercomplex system material gas; furthermore, nanoconstructions of products can be controlled by properly changing synthesis conditions, which implies that CVD is the optimum method for synthesizing fine composites.

CVD introduces a material gas into a heated area to cause various chemical reactions. As a result, when a substrate is used, films or bulky deposits can be obtained, while, when a substrate is not used, fine particles can be obtained<sup>(56)</sup>. In this case, making the material gas hypercomplex enables ceramic fine composites to be synthesized on an in-situ basis<sup>(57)</sup>.

The authors have so far synthesized a large number of fine composites with C,  $\text{Si}_3\text{N}_4$ , SiC and BN as parent phases using CVD<sup>(9)</sup>. For example, in the case of C-SiC with disc-shaped  $\beta$  type SiC, several tens of nanometers in size dispersed in C, the oxidation resistance of C remarkably improved<sup>(58)</sup>. With respect to  $\text{Si}_3\text{N}_4$ -C with noncrystalline C, several hundreds of nanometers in diameter

dispersed in noncrystalline  $\text{Si}_3\text{N}_4$ , C particles formed a three-dimensional network, and the conductivity was increased by 10 digits by adding only 0.2 mass percent C<sup>(59)</sup>.  $\text{Si}_3\text{N}_4$ -BN, with noncrystalline  $\text{Si}_3\text{N}_4$  and irregular layered BN laminated about 100 nm thick, is transparent and can retain the translucency at a high temperature of about 1870 K<sup>(60)</sup>. With regard to  $\text{Si}_3\text{N}_4$ -TiN with fibrous TiN, several nanometers in diameter, dispersed in  $\beta$  type  $\text{Si}_3\text{N}_4$ , the addition of only 0.05 volume percentage TiN caused the thermal conductivity to decrease to one-tenth<sup>(61)</sup>. High toughness was achieved with regard to SiC-TiC with granular TiC several micrometers in size dispersed in SiC. Figure 7 (not reproduced) shows the status of crack occurrence in the periphery of an impression caused by an indenter pressed into the SiC-TiC surface<sup>(62)</sup>. While multiple microcracks can be observed in the periphery of the impression, no long cracks running from the four corners of the impression can be observed, thereby showing that the progress in cracks is stopped by dispersed phases. The  $K_{IC}$  value is estimated at above  $10 \text{ MPa}\cdot\text{m}^{1/2}$ <sup>(62)</sup>.

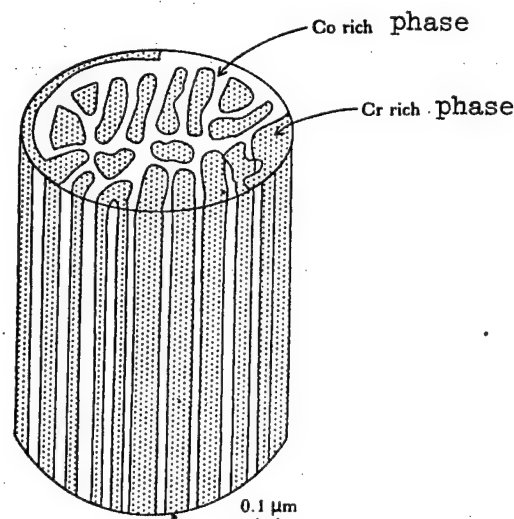


Figure 6. Microstructure of a Carbon-Added Co-Cr Film<sup>(42)</sup>  
(carbon content, 0.25 atm%)

## 5. Design of CVD Fine Composites

CVD is a method for synthesizing materials making use of chemical reaction between material gases<sup>(63)</sup>, with heat used as energy to promote reaction. Therefore, the driving force for reaction is thermodynamic parameters, such as  $\Delta G$ , and materials are synthesized in the state relatively close to equilibrium. For this reason, the optimization of CVD conditions has been attempted many times using thermodynamic calculation<sup>(64)</sup>.

Many synthesis conditions must be controlled since hypercomplex-system material gases are used particularly for synthesizing CVD fine composites. Therefore, some guidelines for material design becomes indispensable and the projection by

thermodynamic calculation is a prospective approach is being demonstrated<sup>(65,66)</sup>. In addition with CVD, the processes related to the kinetics, such as gas flow, substance transport, chemical reaction and crystal growth, are important and, particularly, these processes are major factors to determine microstructures of products<sup>(67)</sup>. Computer analysis of gas flow and film forming speed has so far been attempted and it is known to be effective for controlling film thickness distribution<sup>(68)</sup>.

With respect to material design of functionally gradient fine composites, too, the optimization of material design is attempted by means of three-dimensional analysis of thermal stress, etc.<sup>(48)</sup> Necessary property values are strength, Young's modulus, thermal expansion coefficient and thermal conductivity. Figure 8 presents thermal stresses occurring in the interior when there is a temperature difference of 1000 K between the two ends of a cylindrical structure 95 mm in ID and 105 mm in OD. The broken line indicates thermal stress of free particles and the solid line of CVD·SiC/C system functionally gradient fine composites<sup>(48)</sup>. It is found that slanting compositions cause thermal stress to decrease notably. In addition, with respect to the synthesis of functionally gradient fine composites produced by CVD, material design is being attempted which relates the factors of material synthesis processes to the above thermodynamics and kinetics with material properties<sup>(48,69)</sup>.

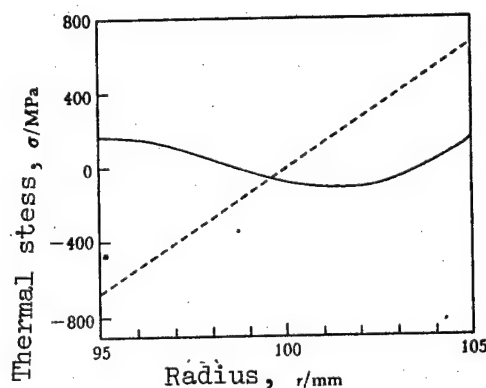


Figure 8. Thermal Stress Occurring in the Interior of the Cylinder<sup>(48)</sup> ID, 95 mm; OD, 105 mm; temperature difference, 1000 K (solid line, CVD·SiC/C functionally gradient fine composite; broken line, CVD·SiC simplex)

Quite recently, the authors have demonstrated that fine compositions of a Y-system superconductive oxide film is remarkably effective for improving superconductive properties<sup>(70)</sup>. A  $\text{YBa}_2\text{CuO}_{7-x}$  film shows such superior properties as about 20 GA/m<sup>2</sup> for a zero magnetic field (77 K) and 0.65 GA/m<sup>2</sup> for 27 T (77 K). As shown in Figure 9 (not reproduced), this film has CuO dispersed in it and a small quantity of a-axis oriented crystals dispersed in the c-axis oriented matrix. An analysis of the nanostructure of this fine composite film is currently under way.

## 6. Conclusion

Functionally gradient composites have been created by the unique design concept based on nanocomposites. As a material for space shuttles in the future, research & development on them has already been energetically promoted as a national project, with studies on material synthesis, functional design and property evaluation actively under way.

A detailed study on nanocomposites has found that the combination of "factors" results in specific properties. The effectiveness of fine composites based on a new concept has been demonstrated by advanced microstructure observation technology and much progress is expected in the future.

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## Future Energy Related Equipment, Materials

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[Article by Masayuki Kamimoto, director of the Energy Material Laboratory, Energy Basic Division, Electrotechnical Laboratory, Agency of Industrial Science and Technology: "Major Next Generation Energy Technologies and Needs for and Current Status of Material Development; Exception for Development of Heat Resistant Energy Materials"]

### [Text] 1. Introduction

Parallel to low-level transition of oil prices, the interest in energy development seemed to be forgotten until recently, as current environmental problems arouses public opinion, the importance of energy technologies is again being recognized. The energy measures being taken are two-fold, in accordance with the environment; they are the development of clean substitute energy and energy saving technologies. With respect to the development of energy technologies with high profitability and efficiency, materials are the key to it in many cases. Energy materials are destined to function under harsh conditions (ultimate environment), which is deeply related to the fact that new energy technology does not appear in a short time. It is deemed that material development takes much time. The focus will be narrowed down to heat-resistant energy materials necessary for high-efficiency energy conversion. In the first place, with respect to major next generation energy technologies, the harsh environment surrounding energy materials and the need for and the current status of the development of energy materials will be described, followed by the expectation for material development in the future.

### 2. Major Next Generation Energy Technologies and Needs for and Current Status of Material Development

#### 2.1. Ceramic Gas Turbine

A gas turbine is a compact energy conversion device capable of high output which rotates a turbine while expanding a high-temperature high-pressure gas into a high-speed gas flow and supplies and generates power to transport. Generally, an approach involving combustion, using compressed air and producing a gas with high temperature, and pressure is employed, finding a wide

range of applications in prime movers for use in aircraft and power generation. An increase in gas temperature and pressure at the turbine inlet and in turbine revolution can contribute to improved efficiency and the miniaturization of a turbine. For this reason, the development, to date, of materials with high temperature and high strength has been promoted.

While the turbine inlet temperature has been on the rise year by year, the useful temperature of materials for gas turbine blades has kept increasing as shown in Figure 1<sup>(1)</sup> due to the development of reinforced superalloys. For a compact gas turbine to achieve the thermal efficiency of above 40 percent, requires improved efficiency of gas turbine factors and turbine inlet temperature of 1300 to 1400°C.

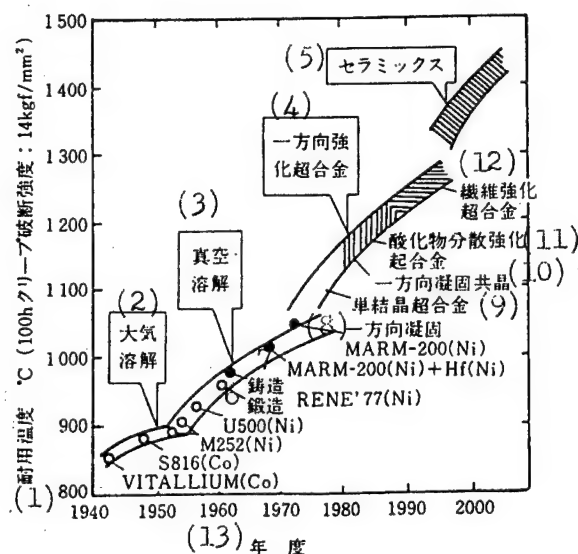


Figure 1. Increase in Useful Temperature of Gas Turbine Blade Materials<sup>(1)</sup>

Key:

- |                                  |   |
|----------------------------------|---|
| 1. Useful temperature            | 8. One-way solidification                 |
| 2. Atmospheric solution          | 9. Single crystal superalloy              |
| 3. Vacuum solution               | 10. One-way solidified eutectic           |
| 4. One-way reinforced superalloy | 11. Oxide dispersed reinforced superalloy |
| 5. Ceramics                      | 12. Fiber reinforced superalloy           |
| 6. Forging                       | 13. Fiscal year                           |
| 7. Casting                       |   |

A superalloy turbine blade currently in use has adopted a complex interior cooling construction, shown in Figure 2, with a view to its use at much higher temperatures than the useful temperature of its material. As long as compact equipment is aimed for, however, it is not necessary to cool or to

reduce a cooling area. To cope with this, ceramics are being used for possible sections. Ceramics are not suitable for parts with complex shapes and their brittleness is a disadvantage. At present, roles are shared by metals and ceramics in cases, as for example, where a stationary blade with silicon nitride caught between the metallic casings is used or ceramics are used only for the rotor<sup>(2)</sup>.

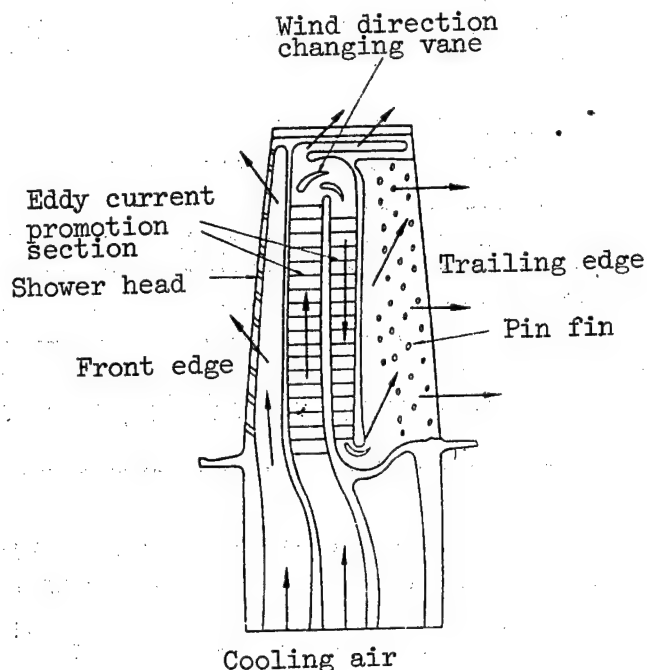


Figure 2. Structural Example of an Air-Cooled Gas Turbine Blade<sup>(1)</sup>

In the United States, following the Advanced Gas Turbine (AGT) Project, the Advanced Turbine Technology Application Project (ATTAP) was started in 1987. The ATTAP is aiming at demonstrating application technology for structural ceramics with the durability potential of 3500 hours (corresponding to 100,000-mile running) at a turbine inlet temperature of  $1371^{\circ}\text{C}$ <sup>(3)</sup>. In Japan, too, the "Ceramic Gas Turbine Technology Development" commenced in fiscal 1988 on the Moonlight Project by the Agency of Industrial Science and Technology, which targets achieving a turbine inlet temperature of  $1350^{\circ}\text{C}$  and thermal efficiency of 42 percent with a 300-kW compact ceramic gas turbine<sup>(4)</sup>. Table 1<sup>(2)</sup> shows examples of properties required for materials that are used for turbine stationary and moving blades. A stationary blade is exposed at the locally highest temperature and requires the most demanding performance against thermal impact and fatigue when a turbine is starts and stops. With a moving blade, the temperature condition is relaxed since temperature becomes uniform due to high-speed rotation, but high strength is required.

When the turbine inlet temperature rises, the temperature of attachments, such as a combustor and a heat exchanger, also rises. To cope with this, combustors using ceramics for parts for use in these attachments require thermal impact, and high temperature resistance. On the other hand, materials with low

coefficient of thermal expansion are desirable for materials for use in heat exchangers. Table 2<sup>(2)</sup> shows promising ceramic parts and their service temperatures. One of the major problems of ceramics is their brittleness and, to cope with this, an attempt of making them composite by means of whisker reinforcement is being made, with no adequate strength and fracture toughness obtained. On the other hand, it has been pointed out that in order to apply such new materials to gas turbines, it will be necessary to develop parts molding technology and parts design technology quite different from conventional methods<sup>(5)</sup>.

Table 1. Examples of Required Values of Material Properties for Design Conditions Pursuing High Performance Aerodynamical Properties<sup>(2)</sup>

Member	Turbine Stationary Blade	Turbine Moving Blade
Working temperature	1350°C	1250°C
Minimum proof strength	400 MPa	600 MPa
Weibull coefficient	20	20
Fracture toughness	10 MPa·m <sup>1/2</sup>	15 MPa·m <sup>1/2</sup>
Thermal fatigue property	1350°C-room temperature 1300 cycles	1250°C-room temperature 1000 cycles

Table 2. Table of Ceramic Parts Materials for Gas Turbine Use<sup>(3)</sup>

Note: \*Marks represent relative total temperature

Part Name	Working Temperature (°C)	Material
Combustor liner	1400	SiC
Turbine scroll	1400	SiC
Gas generator nozzle	1400	SiC
Gas generator turbine rotor	*1320	Sialon, Si <sub>3</sub> N <sub>4</sub>
Gas generator shroud	1300	Si <sub>3</sub> N <sub>4</sub>
Gas generator back plate	1300	Si <sub>3</sub> N <sub>4</sub>
Interturbine duct (inner)	1230	Si <sub>3</sub> N <sub>4</sub>
Interturbine duct (outer)	1230	Si <sub>3</sub> N <sub>4</sub>
Power turbine nozzle	1230	Si <sub>3</sub> N <sub>4</sub>
Power turbine rotor	*1100	Sialon, Si <sub>3</sub> N <sub>4</sub>
Heat exchanger core	990	AS, MAS
Exhaust diffuser	990	Si <sub>3</sub> N <sub>4</sub>

## 2.2. MHD Power Generation

MHD power generation is a method for directly generating power, making use of the generation of an electric field flowing vertically to the direction of the

magnetic field, according to Faraday's law, when the conductive fluid flows across the magnetic field. Vapor power generation or combined power generation with a gas turbine enables extremely high efficiency to be obtained. MHD power generation, using a gas for working fluid, includes the open cycle and the closed cycle.

As shown in Figure 3<sup>(6)</sup>, the open cycle preheats air to 2000 K using a combustion gas from an MHD generator and burns a fossil fuel with the preheated air to obtain a gas of 3000 K. In order to provide the gas with conductivity, a potassium compound is introduced as a seed to lead to the power generating channel. The combustion gas from the generator preheats air and then vapor is generated with the boiler. With such a system, the generating efficiency is expected to reach 60 percent. The greatest advantage of the open cycle is that coal can be directly burnt without gasifying it. On the other hand, with the closed cycle using a rare gas, despite working temperature being as low as 2000 K, the generating efficiency of above 55 percent is expected. Therefore, the service condition for the open cycle is much severer in terms of material.

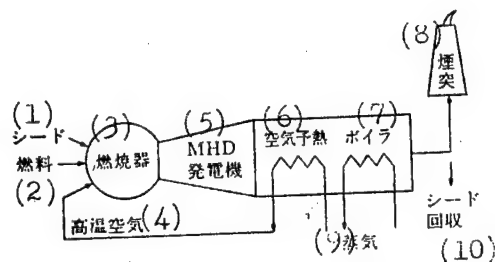


Figure 3. Basic Construction of Open Cycle MHD Generator<sup>(6)</sup>

Key:

- |                         |                    |
|-------------------------|--------------------|
| 1. Seed                 | 6. Air preheating  |
| 2. Fuel                 | 7. Boiler          |
| 3. Combustor            | 8. Chimney         |
| 4. High temperature air | 9. Vapor           |
| 5. MHD generator        | 10. Seed retrieval |

The open cycle currently adopted by the Soviets preheats air to about 700°C using a metallic bulkheat heat exchanger and causes the temperature to reach 2000 K by separately burning a clean fuel. This causes the efficiency to decrease to 45 to 48 percent<sup>(6)</sup>. The heat storage substance, insusceptible to the corrosion by a seed substance at 2000 K can be developed, and the efficiency can be close to an estimated value if they could also avoid clogging.

Since a combustion furnace has only to meet a simple requirement of burning at high temperature and pressure, slag component can be prevented from being attacked by vapor by means of cooling the furnace wall. On the other hand, materials for use in generating channels must meet extremely severe requirements since a generating channel needs to fulfill the function of power generation. As shown in Figure 4,, a generating channel comprises multiple corresponding electrodes and insulators.



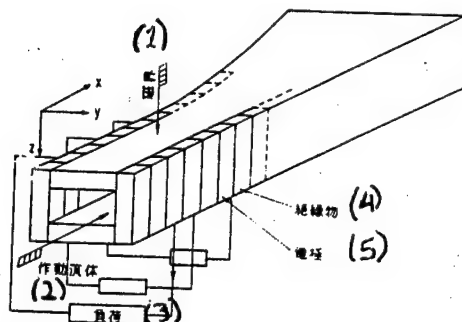
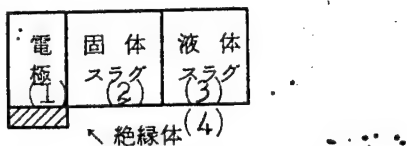


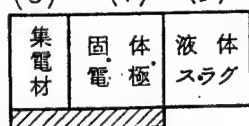
Figure 4. Conceptual View of MHD Power Generating Channel Construction

Key:

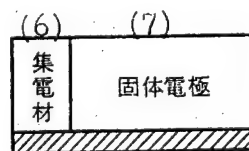
- |                      |              |
|----------------------|--------------|
| 1. Magnetic field    | 4. Insulator |
| 2. Operational fluid | 5. Electrode |
| 3. Load              |              |



(a) コールド壁 (1,000 K 以下)  
(6) (5) (7) (3)



(b) セミホット壁 (1,500-1,800 K)  
(8)



(c) ホット壁 (1,800 K 以上)  
(9)

Key:

- |                                |
|--------------------------------|
| 1. Electrode                   |
| 2. Solid slag                  |
| 3. Liquid slag                 |
| 4. Insulator                   |
| 5. Cold wall (below 1000 K)    |
| 6. Current collecting material |
| 7. Solid electrode             |
| 8. Semihot wall (1500-1800 K)  |
| 9. Hot wall (above 1800K)      |

Figure 5. Classification of MHD Power Generating Channel Electrode Walls (7)

- (a) コールド壁 (1000 K 以下). (5)  
(b) セミホット壁 (1500~1800 K). (8)  
(c) ホット壁 (1800 K 以上). (9)

For electrode wall design, there are three ideas shown in Figure 5<sup>(7)</sup>, based on the setting of surface temperature. With the cold wall type, the wall surface is retained at below 1000 K to form solidified slag phases. The solidified slag phase is superior in durability performance, but great in thermal loss and complex in the cooling structure. The current concentration resulting from interelectrode defective insulation, high internal resistance of solid phase slag and the heterogeneity of solid slag creates such problems as the consequent reaction with electrode materials, the corrosion in electrode with electrode materials, the corrosion in electrode materials caused by  $K^+$  deposited on the cathode, electrochemical reaction on the anode, the occurrence of arc, etc.

With respect to the cathode, materials have a wide range of selection among heat-resistant alloys, cermet-system materials and water-cooled electrodes, capped by a copper-tungsten alloy or molybdenum. These have demonstrated adequate durability. On the other hand, AVCO Corp.'s electrodes and platinum- or high chrome steel-capped water-cooled copper electrodes (anodes) tested by the Electrotechnical Laboratory, involve a method for purposely generating arc, withstanding the oxidation and corrosion atmosphere resulting from  $O^{2-}$  and  $S^{2-}$  by means of platinum and high chrome steel, and removing thermal input caused by arc discharge by means of the copper base<sup>(8)</sup>. Since platinum is a rare resource, it is hoped to be developed into a substitute material.

With a semi-hot wall type, making wall surface temperature higher than the melting temperature of slag (1500-1800 K), prevents internal resistance caused by solid-phase slag, from increasing and enables the efficiency to increase<sup>(9)</sup>. On the other hand, the wall material is exposed to the great temperature gradient and forced to coexist with liquid slag containing potassium. Along with being energized, the cathode side is polarized to the reducing atmosphere and the anode side to the oxidizing atmosphere. An electrode material needs stability in the wide oxygen partial pressure and high conductivity. In the case of Mark II of the Electrotechnical Laboratory, the calculated maximum heat flux of the upstream side of the  $MgO$  insulating wall for a surface temperature of 1700 K exceeds  $150 \text{ W/cm}^2$ <sup>(10)</sup>. Therefore, problems of insulating wall materials include bonding with dissimilar materials and thermal stress fracture, in addition to chemical and electric damage.

Evaluation of various cermets and ceramics, as electrodes, has been conducted to date. It has been made clear that, compared to the alloy system, the cermet system (Fe-radical metals added by  $Al_2O_3$ ) or  $ZrO_2$  ( $ZrO_2-LaCaCrO_3$ ,  $ZrO_2-CeO_2$ , etc.),  $SnO_2$  possesses more superior properties in the temperature area of 1300 to 1500 K<sup>(10)</sup>. A study is being conducted on composites, with a  $ZrO_2-CeO_2$  system matrix added by carbon fibers, and  $SiC$  whiskers with a view to ceramic electrodes for cathode use capable of using at 1000 to 1800 K<sup>(10)</sup>. With regard to an insulating wall, good results have been achieved using a method for bonding  $SiC$  to the copper-made C type cooling base via a  $CuC$  cushioning material<sup>(11)</sup>.

With the hot wall type, the wall temperature is increased to above 1800 K to prevent slag from depositing. There are no problems which are caused by slag, but new problems occur, such as the evaporation of the wall material and the corrosion against the cathode surface in the plasma state such as  $K^+$ , also, the temperature gradient further increases. Studies on materials in this temperature area have not made much progress.

### 2.3. Solid Electrolyte Type Fuel Cell<sup>(12,13)</sup>

A solid electrolyte type fuel cell called a third generation fuel cell is positioned as a next generation fuel cell. It is operated at about 1000°C since zirconia, which is used, has large resistance. It has such advantages, besides being completely solid, as high electrode activity, no need of a reformer and a CO transformer against a coal gas containing CO, which enables high-temperature thermal radiation to be utilized for power generation and thermal application.

Figure 6<sup>(12)</sup> illustrates the construction of WH Corp.'s cylindrical type cell with long time operational performance. Air ( $O_2$ ) is introduced from the alumina thin tube inserted into the porous zirconia tube and a fuel ( $H_2$ ) flows outside of the tube. These tubes are bundled to be in series and parallel as shown below.

The individual materials need to withstand high temperature and, since they are in contact with one another and in the oxidizing or reducing atmosphere, it is necessary to take the chemical reactivity and thermal expansion quality into account. Other requirements include that pneumatic electrodes must be porous and that a separator has high electronic conductivity with no ionic conductivity. Table 3<sup>(12)</sup> shows prospective candidate materials.

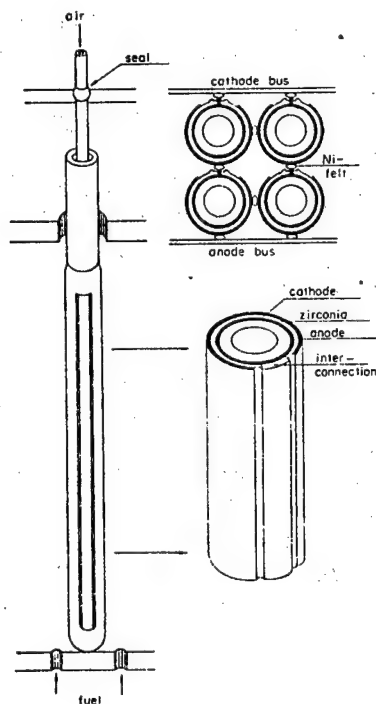


Figure 6. WH's Cylindrical Solid Electrolyte Fuel Cell<sup>(12)</sup>

Table 3. Candidate Materials for Use in Solid Electrolyte Fuel Cell<sup>(12)</sup>

Parts	Candidate Material	Prospective Material	Reason for Selection
Electrolyte	Zirconia	Zirconia	Chemical stability
	Ceria [phonetic]		High ionic conductivity
	Bismuth oxide		Low electronic conductivity
	Thoria		Strength
Anode	Ni, Co	Ni-ZrO <sub>2</sub>	Low polarization ability
			Sulfur resistance
			Reformer catalytic ability
Cathode	Perobslote [phonetic]	LaMnO <sub>3</sub>	Chemical stability
	Various metallic oxides		Low polarization ability
			High electronic conductivity
Separator	Perobskite [phonetic]	LaCrO <sub>3</sub>	High ionic conductivity
	Spinel		Low ionic conductivity
	Platinum		Chemical stability
			(oxygen resistance, hydrogen resistance)

While problems of WH's cell, in terms of material, seem to have almost been solved, however, some problems remain in terms of production cost, increased internal resistance due to elongated current passage (related to efficiency) and energy density. These problems can be solved by adopting a plate type (Figure 7)<sup>(12)</sup> or a monolithic type (Figure 8)<sup>(12)</sup>. As can be easily imagined from their constructions, the production of zirconia self-supported films with high strength, large area and airtight gas sealing will be extremely difficult.

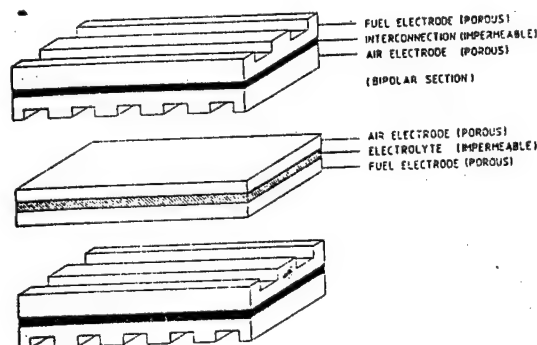


Figure 7. Typical Figure of a Plate Type Solid Electrolyte Fuel Cell<sup>(12)</sup>

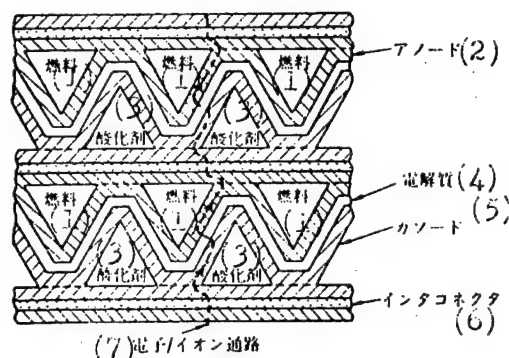


Figure 8. Gas Combined Flow Monolithic Solid Electrolyte Fuel Cell<sup>(13)</sup>

Key:

- |                |                         |
|----------------|-------------------------|
| 1. Fuel        | 5. Cathode              |
| 2. Anode       | 6. Interconnector       |
| 3. Oxidizer    | 7. Electron/ion passage |
| 4. Electrolyte |                         |

#### 2.4. AMTEC<sup>(14)</sup>

Alkali metal thermoelectric conversion (AMTEC) is thermoelectric conversion using sodium ionic conductive  $\beta''$ -alumina. Figure 9 illustrates the principle of operation. The difference in vapor pressure between the high temperature side (873-1273 K) and the low temperature side (373-773 K), plays the role of the driving force which moves sodium from the high temperature side to the low temperature side.  $\beta''$ -alumina placed between those different temperatures being conductive to sodium ions, connecting it to the load from either end causes power to be generated. Since sodium vapor condenses on the low temperature side, circulating liquid sodium to the high temperature side with the electromagnetic pump, enables power to be generated in succession. With no portable section, high output density and the expectation for high efficiency, a study on AMTEC as a dispersed power generating system for ground and space use is being promoted.

The generating efficiency of AMTEC increases as the high temperature increases. Therefore, it is desirable to operate it at the highest temperature of the material. The electrode being required to withstand high temperature, not to react with sodium, to allow sodium vapor to pass and to be low in electric resistance, a porous thin film, one of Mo, etc. produced by sputtering, is used. The long time durability of  $\beta''$ -alumina in these electrode materials and sodium is an important problem to be studied in the future.

Constructing a sodium loop requires sealing the heat resistant metallic materials  $\beta''$ -sodium at a high temperature of about 1300 K. If this technology fails to be developed a review of the device structure will have to be conducted.

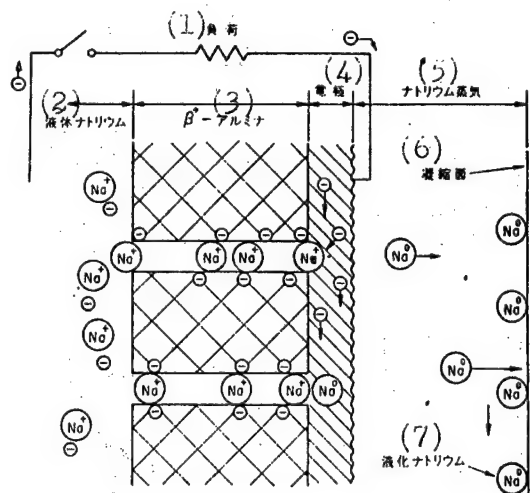


Figure 9. Principle of Operation of AMTEC<sup>(14)</sup>

Key:

- |                      |                         |
|----------------------|-------------------------|
| 1. Load              | 5. Sodium vapor         |
| 2. Liquid sodium     | 6. Condensation surface |
| 3. $\beta$ "-alumina | 7. Liquified sodium     |
| 4. Electrode         |                         |

## 2.5. Latent Heat and Heat Reserve for Use in Space Solar Thermal Electric Conversion

It is considered that various large-size structures led by a space station on a relatively low orbit about 450 km high will require much power in the future. Space solar thermal electric conversion has not yet been demonstrated, but high efficiency can be expected since, unlike on the ground, strong sunshine can be obtained in space. In order to obtain power when the sun is behind the earth, a heat storage device will be indispensable. Since, in space, the top priority is given to high heat storage density per unit weight, latent heat and heat reserve are the most suitable. The turbine inlet temperature of an operative medium in space solar thermal electric conversion being about 800°C, lithium fluoride (LiF: melting point, 845°C), etc. will be a prospective material for latent heat and heat reserve.

The items to be considered for using fused salt for an actual heat storage device (receiver) (Figure 10) include: (1) Corrosivity, (2) thermal stress accompanying changes in volume of fused salt, (3) a decrease in heat transfer performance resulting from void generated by fusion and solidification of fused salt under microgravitation. The receiver performance can be substantially improved by overcoming these problems by impregnating fused salt in porous ceramics<sup>(15)</sup>.

Porous (porosity, about 40 percent)  $\beta$ -SiC and LiF composites with high heat resistance, superior corrosion resistance and high thermal conductivity showed

good thermal and configurational stability, while vapor pressure of LiF in the service temperature area cannot be ignored, and preventing LiF from vaporizing remains a major problem<sup>(16)</sup>. Airtight gas seal creates a critical problem in this respect. It is necessary to increase the porosity to about 70 percent in the future<sup>(17)</sup>. To cope with this, a problem of the strength of porous ceramics withstanding repeated fusion and solidification of fused salt must be solved.

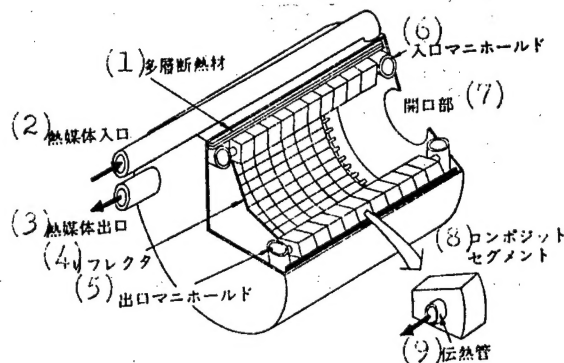


Figure 10. Receiver Using Fused Salt/Ceramics Composite Heat Regenerator

Key:

- |                                |                      |
|--------------------------------|----------------------|
| 1. Multilayered heat insulator | 6. Inlet manifold    |
| 2. Thermal medium inlet        | 7. Opening           |
| 3. Thermal medium outlet       | 8. Composite segment |
| 4. Reflector                   | 9. Conductive tube   |
| 5. Outlet manifold             |                      |

### 3. Expectation for Developing Heat Resistant Energy Materials

The above are descriptions of the current status of material development with respect to typical examples of next generation energy devices to be used at high temperature. Materials used for these devices need not only to withstand high temperature under such harsh environment as high thermal flux, large temperature difference, strong magnetic and electric fields and oxidizing, reducing and corrosive atmosphere, but to meet various functions required. While so-called new materials show superior performance with respect to certain functions, they are a few levels below with regard to other properties in comparison to conventional materials in many cases. For the time being, roles will be shared by new and conventional materials and efforts will be made for improving the performance of devices by means of design to utilize their individual characteristics.

Depending technologies, sometimes demands for materials are quite different from the reality, while some demands seem to meet their needs. In the latter cases, too, a study on long time durability often needs to be carried out. Since the profitability is important for energy devices in general, it may be necessary to review and redevelop device structures and their processes.

The first conceivable properties expected for heat resistant materials are strength and thermal impact resistance at high temperature; however, every material is used in coexistence with other materials in many cases. Particular problems with such cases will be the difference in chemical reactivity and thermal expansion coefficient. Bonding and airtight gas seal of dissimilar materials are also important problems.

With respect to the direction of new material development, it is expected that roles will be shared by various materials. New materials will be developed by the atomic-level combination, to meet the needs of next generation energy devices. The combination of the process in some form will be effective means.

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